Determination of Trace Elements in Crude Oils by ICP-MS Using Detergent Microemulsion

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A thesis submitted to the Faculty of Health and Wellbeing of Sheffield Hallam University in partial fulfillment of the requirements for the degree of Master of Philosophy

November 2008

Abbreviations

API	American Petroleum Institute
UOP	Universal Oil Product
ppm	Parts Per Million
LPG	Liquefied Petroleum Gas
FAAS	Flame Atomic Absorption Spectrometry
ETAAS	Electrothermal Atomization In Graphite Furnace
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
VG	Vapor Generation
IBMK	Isobutyl Methyl Ketone
BA	Butyl Acetate
ETV	Electrothermal Vaporization
USN	Ultrasonic Nebulizer
MIBK	Methyl Isobutyl Ketone
SPL	Solvent Plasma Load
NaDS	Sodium Dodecylsulphate
HLB	Hydrophile-Lipophile Balance
SDS	Sodium Dodecylsulphate
ETV ICP-MS	Electrothermal Vaporization Inductively Coupled Plasma-Mass Spectrometer

K	Kelvin
TDS	Total Dissolved Solid
bbl	Barrels
bbl/d	Barrels Per Day
HP	Hewlett Packard
RF	Radio Frequency Power
Sp.g	Specific Gravity
EDS	Emulsion Droplet Size
CRM	Certified Reference Material
LOD	Limits of Detection
LOQ	Limits of Quantification
RSD	Relative Standard Deviation
SD	Standard Deviation
r^2	Correlation Coefficient
n	Number of Replicates

Abstract

A method was developed and evaluated in terms of its analytical performance for the determination of Ti, V, Cr, Mn, Ni, Cu, Mo, Cd, Sn and Pb concentrations in three Libyan crude oil samples using ICP-MS. The samples were introduced to the plasma after the formation of microemulsions in which Triton X-100 was used as the emulsifier and tetralin was the co-solvent with the addition of nitric acid in order to enable calibration with aqueous standard. The validity of the method was proven by three different traditional sample preparation protocols (dry ash, wet digestion and microwave digestion) and good agreement was obtained between the results using the proposed and comparative procedures. The accuracy was confirmed by analysing two different certified reference materials (Used Oil HU-1 from SCP science and Wear Metals in Lubricating Oils 1084a from NIST). The recoveries ranged from 100.1% to 119.9 % for all elements and 85.1 % for Cr in Used Oil HU-1 and from 84.8 % to 100.1 % for all elements and 79.1 % for Cr in 1084a NIST. The precision of the method was < 5% for all elements, except for Cr which was 30.9 %. The limits of detection based on 3 times standard deviation of the blank (10 replicates), were ranging from 0.1 to 0.7 ng g^{-1} for all elements and 4.8 ng g^{-1} for Cr. The limits of quantification based on 10 times standard deviation of the blank (10 replicates) ranged between 0.2 to 2.4 ng g^{-1} and 16.1 ng g^{-1} for Cr. Satisfactory recoveries were obtained when 2 µg L^{-1} and 10 µg L^{-1} multielement spikes were used to test the accuracy of the developed method. The method has proven to be reliable, and can be used in routine analysis in laboratories where there is a high throughput of the sample.

Dedication

I would like to dedicate my thesis to my father and mother who offered me unconditional love and support throughout my life. To my dear husband, without his support, and gentle encouragement, I wouldn't have finished this thesis, and to a loving family that just never stopped giving of themselves in countless ways, both direct and indirect.

Acknowledgements

Praise and gratitude be to ALLAH, Almighty, without whose gracious help it would have been impossible to accomplish this work.

I would like to acknowledge and extend my gratitude to my supervisor Dr. Philip Gardiner, for his guidance and helpful suggestions throughout this study and for his vital encouragement and support. My thanks to Professor Malcolm Clench, for his understanding and assistance. I am also deeply thankful to Professor Nicola Woodroofe, for her efforts to afford a supportive environment for students in BMRC to finish their studies. Many thanks to Dr. Peter Drew, for his invaluable advices and supplies of references. And to the two helpful ladies, Marguerite Lyons and Sarah Wright for the help and inspiration they extended.

My gratitude to Libyan Petroleum Institute for giving me this opportunity for studying MPhil as a part time student in Sheffield Hallam University.

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Chapter 1

1. Introduction

1.1 Occurrences and Importance of Crude Oil and Fractions

Land, sea and air transportation depend almost entirely on products refined from crude oil. Refineries convert about three quarters of the crude oil into transportation fuels. Other refined oil products are used to heat homes and buildings, generate electricity, and in the manufacture of lubricants, waxes, plastics, synthetic rubber and asphalt.

The crude oil industry provides thousands of jobs in exploration, production, transportation, refining, distribution and marketing. It also supports a variety of technological research and development.

The origin of crude oil has been the subject of considerable debate, but it is now accepted that it is organic in origin and that the raw material was the bodies of marine organisms together with water-deposited plant life. Oil was formed from the remains of those organisms and plants that lived millions of years ago in a marine environment. Over the years, the remains were covered by layers of mud. Heat and pressure from these layers helped the remains turn into crude oil [1].

1.2 Classification of Crude Oil

Crude oils in general are complex mixtures containing different hydrocarbons associated with very small amounts of nitrogenous substances and variable amounts of organic sulphur compounds. These hydrocarbons may be paraffinic, olefinic, naphthenic and aromatic in character [1,2]. Crude oil ranges in consistency from water to tar like solids, and in colour from clear to black. An "average" crude oil contains about 83.9 % - 86.8 % carbon, 11 % - 14 % hydrogen, 0.06 % - 8.0 % sulfur, 0.02 % - 1.7 % nitrogen, 0.08 % -1.82 % oxygen, 0.00 % - 0.14 % metals, and salts [1].

Relatively simple crude oil assays are used to classify crude oils as paraffinic, naphthenic, aromatic or mixed. One assay method (United States Bureau of Mines) is based on distillation, and another method (UOP "k" factor) is based on specific gravity and boiling points [1]. Crude oils are also defined in terms of API (American Petroleum Institute) gravity. The higher API gravity is, the lower the specific gravity and hence the lighter the crude. The heavier crude oil contains more sulphur which makes it more difficult and expensive to turn it into usable refined products. Crude oils that contain appreciable quantities of hydrogen sulphide or other reactive sulphur compounds are called "sour". Those with less sulphur are called "sweet".

The viscosity of crude oils varies greatly even with oils from the same district. It increases with rise of specific gravity; the higher value for both being dependent mainly upon the presence of heavier hydrocarbons, but no connection can be traced between viscosity and specific gravity, oils of the same specific gravity varying widely in viscosity. Increase of temperature causes a rapid decrease in the viscosity

and a rise of a few degrees will often cause a sluggish oil to flow freely. The pour point of an oil is the lowest temperature at which it will pour or flow readily.

Density is one of the principle physical properties in classifying crude oils and it is defined as the mass per unit volume. Crude oil density is temperature-dependant, decreasing as temperature rises. Generally, paraffinic hydrocarbons have low densities, naphthenic, and olefinic hydrocarbons intermediate densities, and aromatic hydrocarbons high densities. The densities of crude oils generally lie in the range 0.79 to 0.95 g/cm^3 [1].

1.3 Chemical Composition of Oil

1.3.1 Hydrocarbons

Crude oil is a mixture of hydrocarbon molecules, containing between 1 to 60 carbon atoms. The properties of the hydrocarbons depend on the number and arrangement of the carbon and hydrogen atoms in the molecules. Hydrocarbons containing up to four carbon atoms are usually gases, those with 5 to 19 carbon atoms are usually liquids, and those with 20 or more are solids. The refining process uses chemicals, catalysts, heat, and pressure to separate and combine the basic types of hydrocarbon molecules naturally found in crude oil into groups of similar molecules. The refining process also rearranges their structures and bonding patterns into different hydrocarbon molecules and compounds. Therefore it is the type of hydrocarbon (paraffinic, naphthenic, or aromatic) rather than its specific chemical compounds that is significant in the refining process.

1.3.2 Nonhydrocarbons

Crude oils contain considerable amount of organic compounds with structures incorporating one or more atoms of sulphur, nitrogen, or oxygen in addition to carbon and hydrogen; and some of these are associated with metals such as vanadium and nickel. Crude oil may also contain relatively minor amounts of suspended inorganic salts (mainly chlorides) and of dissolved elemental sulphur and hydrogen sulphide.

1.3.2.1 Sulphur Compounds

Sulphur may be present in crude oil as hydrogen sulphide (H_2S), as compounds (*e.g.* sulphides, mercaptans, disulphides, thiophenes,.....*etc.*) or as elemental sulphur. Each crude oil has different amounts and types of sulphur compounds, but as a rule the proportion, stability, and complexity of the compounds are greater in heavier crude-oil fractions. Hydrogen sulphide is a primary contributor to corrosion in refinery processing units. Other corrosive substances are elemental sulphur and mercaptans. Petroleum products containing sulphur compounds produce undesirables such as sulphuric acid and sulphur dioxide.

1.3.2.2 Oxygen Compounds

Oxygen compounds such as phenols, ketones, and carboxylic acids occur in crude oils in varying amounts. The total amount of combined oxygen in crude oils is relatively low, ranging from traces to 2 % by weight [1]. Oxygen mainly exists in the form of carboxylic acid in the low and medium boiling range distillate fractions. For this reason, and instead of determining the total oxygen content, the determination of the acidity of the fraction becomes most significant. Consequently, paraffinic crudes and their distillate fractions are low in acidity, where as asphaltic crudes like

Romanian, Venezuelan, Californian contain considerable amounts of acids ranging from 0.6 to 1.0 % by weight or higher [1].

1.3.2.3 Nitrogen Compounds

Organonitrogen compounds are present in traces in the lighter fraction of crude oil; their concentration increases with increasing boiling point and reaches a maximum in asphaltic distillation residues. They are relatively stable towards heat and do not decompose under refinery conditions, so their presence causes problems. Metalloporphyrins are the most important organonitrogen compounds in crude oils. Nickel and vanadium porphyrins are commonly the most abundant in crude oil and used as geochemical biomarkers because they are fairly ubiquitous in nature. At the same time, they cause problems for they poison catalysts used in refinery processes. Nitrogen oxides are formed in process furnaces. The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion.

1.3.2.4 Salts

Crude oils often contain inorganic salts such as sodium, magnesium and calcium chloride in suspension or dissolved in entrained water (brine). These salts must be removed or neutralized before processing to prevent catalyst poisoning, equipment corrosion, and fouling. Salt corrosion is caused by the hydrolysis of some metal chlorides to hydrogen chloride (HCl) and the subsequent formation of hydrochloric acid when the crude is heated. Hydrogen chloride may also combine with ammonia to form ammonium chloride (NH_4Cl), which causes fouling and corrosion.

1.3.2.5 Carbon Dioxide

The decomposition of bicarbonates present in or added to crude oils, or from the steam used in the distillation process, produces carbon dioxide.

1.3.2.6 Trace Metals

Numerous trace elements have been detected in crude oils besides nitrogen, oxygen and sulphur. Of the many metals listed (arsenic, barium, calcium, chromium, copper, iron, lead, magnesium, manganese, nickel, silver, titanium, vanadium,... *etc.*), nickel and vanadium are the most abundant. Their concentrations depend on the source of the crude oil and can range between $< 1\ \mu g\ g^{-1}$ to more than $1300\ \mu g\ g^{-1}$.

They have been used as biomarkers to provide information on the depositional environment of the source rocks, determine the type of organic source material, estimate sediment or oil maturity, or to correlate crude oils with other oils or potential source rocks [3]. The chemical identity of these geological markers known as petroporphyrins, varies between sources depending upon the biological conditions inherent to each site. Vanadium / Nickel ratios do not change with the biodegradation or weathering of an oil seep [4,5] therefore each oil contains unique petroporphyrins (fingerprint) which link the sample to its geographic origins. Consequently, oils from different origins can be easily distinguished. The stability of these compounds enables matching oil spills to their sources even years after the spill occurred [6]. Nickel and vanadyl porphyrin concentrations vary depending on the source of the crude oil. It is indicated that vanadyl porphyrins are commonly more abundant in heavy crude oils and the reverse is generally the case for light crude oils [7].

Table 1 shows the variation in trace element concentrations even among oils from the same basin. West Canada basin was chosen to demonstrate the mean concentration of elements in one basin [3].

Table 1. The mean concentration of some trace elements of West Canada basin with their ranges in ppm [3].

Element	Mean concentration ppm	Range ppm
S %	0.83	0.05-3.9
V	13.6	0.1-177
Ni	9.38	0.1-74.1
Fe	10.8	0.1-254
Co	0.054	0.0002-2.0
Cr	0.093	0.005-1.68
Mn	0.01	0.003-3.85
Zn	0.459	0.025-5.92
As	0.111	0.002-1.99
Sb	0.006	0.0001-0.035
Se	0.052	0.003-0.511
Hg	0.051	0.002-0.399
Na	3.62	0.01-64.7
Cl	39.3	0.1-1010
Br	0.491	0.002-12.5
I	0.719	0.01-9.0

1.4 Petroleum Refining Operations

Petroleum refining begins with the distillation, or fractionation, of crude oils into separate hydrocarbon groups. The resultant products are directly related to the characteristics of the crude oil processed. Most distillation products are further converted into more usable products by changing the size and structure of the hydrocarbon molecules through cracking, reforming, and other conversion processes. These converted products are then subjected to various treatment and separation processes such as extraction, hydrotreating, and sweetening to remove undesirable constituents (*e.g.* sulphur, hydrogen sulphide, ammonia) and improve product quality. Figure 1 shows the distillation units at the Azzawiya oil refinery.

Figure. 1 Distillation Units at the Azzawiya oil refinery [8]

1.4.1 Refining Operations. Petroleum refining processes can be separated into four basic areas:

1.4.1.1 Fractionation (distillation): Crude oil is separated in atmospheric and vacuum distillation towers into groups of hydrocarbon compounds of different boiling-point ranges called "fractions" (Figure 2).

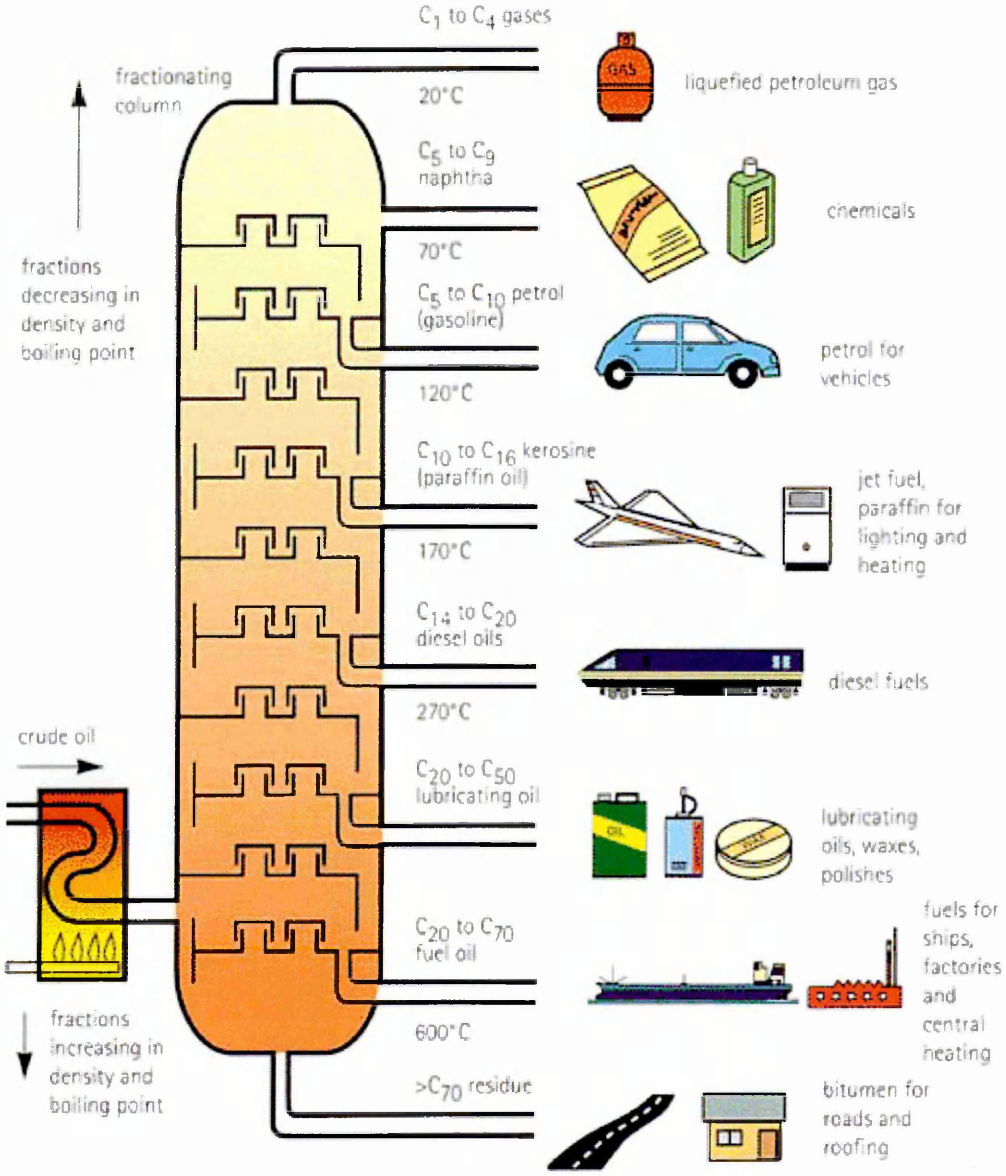


Figure. 2 Diagram showing the fractional distillation process and the refinery products at given temperatures [9].

1.4.1.2 Conversion processes change the size and /or structure of hydrocarbon molecules. These processes include:

- **Decomposition** (dividing) by thermal and catalytic cracking to augment the yield of gasoline.
- **Unification** (combining) through alkylation and polymerization such as the use of polymerization of olefins which is effective in the production of iso-paraffins of high knock-rating by which the gasoline is characterized.
- **Alteration** (rearranging) with isomerization and catalytic reforming that converting straight chains to branches such as converting butane or pentane to isobutane or isopentane.

1.4.1.3 Treatment. This process prepares the hydrocarbon stream for additional processing and to prepare finished product. It includes the removal or separation of aromatics and naphthenes as well as impurities and undesirable contaminants such as H_2O, salts and sulphur compounds.

1.4.1.4 Formulating and Blending. In this process hydrocarbon fractions, additives, and other components are mixed and combined to produce finished products.

1.4.2 Major Refinery Products

The major refinery products are liquified petroleum gas (LPG), gasoline, kerosene, diesel oil, petrochemicals and lubricants, fuel oil and residue.

1.5 Elemental Determinations by Atomic Spectrometry

Information on trace element concentrations in crude oil is very important for the geochemical characterization of source rocks and basins and for corrective actions during oil production and refining (*e.g.* prevention of scale formation and catalyst poisoning, corrosion and pollution control) [3,10,11].

Trace metals occur in crude oil partly as organometallic compounds from which the geoporphyrins of V, Ni, Cu, and Zn have been identified [12-15]. Iron, Sr and Mn contamination could have entered the oil during migration or as pollutants during oil extraction. The elements Mo and Cr are of biological origin [13].

There are three major types of spectrometric methods for identifying the elements present in samples of matter and determining their concentrations; optical spectrometry, mass spectrometry, and X-ray spectrometry [16].

Atomic spectrometric techniques have been used to determine trace elements, among which are flame atomic absorption spectrometry (FAAS), electrothermal atomization in graphite furnace (ETAAS), inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS). FAAS is a well established and accessible technique, less prone to spectral interferences in comparison to ICP-OES and ICP-MS, however, the detection limit is still poor for a series of elements for many applications in crude oil such as As, Sb, Se, Hg and Sn [11,17]. Electrothermal atomization in a graphite furnace (ETAAS) and Vapor generation techniques (VG) overcome the sensitivity limitations of FAAS. Amorim *et al.* [18] reported that oil samples might be analyzed directly by ETAAS if low-temperature losses of volatile compounds such as vanadium compounds are

avoided.

The behaviour of various organic solvents and analytes in ETAAS has been studied by Tserovesky and Arpadjan [19] who found that a high charring temperature is necessary to reduce the nonspecific absorbance. For the influence of the complexing agent, they reported it is insignificant while the effect of the nature of the solvent is more pronounced for toluene and xylene in comparison with IBMK and BA.

A Perkin-Elmer HGA-700 graphite furnace was used, with tungsten impregnated graphite tube and using Pd as the chemical modifier in the organic medium. Analyzing crude oil directly using little or no sample preparation is most suitable for graphite furnace atomic absorption spectrometry although the organic sulphur content in heavy oils may influence the determination of vanadium [20].

Compared to AAS, ICP-OES offers a wider linear dynamic range, and several elements can be determined simultaneously. This property is very important for the multielement analysis of very small samples [16,18,21]. The high viscosity of petroleum and many of its derivatives and the flammability of the lighter fractions make it very difficult to analyse these samples directly by ICP-OES or ICP-MS [11,18,21,22]. As a result, the aspiration of organic liquids into the plasma normally requires additional equipment or sample pretreatment in order to maintain plasma stability, reduce carbon build up and minimize background interferences. Electrothermal vaporization (ETV) [18], ultrasonic nebulization (USN) [23] or introduction of oxygen to the plasma [21], have been used when introducing crude oil or its derivatives to the plasma in order to reduce molecular band emissions and prevent carbon build up.

Despite the spectral interferences and the high cost of ICP-MS, it is considered to be an attractive technique for the determination of trace element concentrations in several organic materials in the petroleum industry, because of its multielement capability and low detection limits. ICP-MS detection limits are in the sub parts per billion range [24] and its ability to measure isotopic ratio is of particular importance [25,26].

Multiple calibration curves are often employed in multielemental techniques such as ICP-OES and ICP-MS to cover the wide range of metal concentration in crude oils, from below ng g^{-1} to hundreds of μg g^{-1} [11]. The standard addition method is recommended for the complex matrices in order to get reliable results [10,23] and the use of internal standardization is essentially for instrumental drift correction and also to account for differences between blanks, calibration standards and samples.

1.6 Sample Pretreatment and Preparation

Sample preparation is the critical step of any analytical protocol, and involves steps from simple dilution to partial or total digestion. Most methods based on atomic spectrometric techniques require sample pre-treatment in order to make them compatible with the employed instrumentation, and also allow easy and efficient calibration procedures to be used. A variety of procedures have been used that are aimed at matrix simplification.

Ashing of the crude oil followed by dissolution of the ash in mineral acids has been used [27]. An investigation of some of the steps involved in the ashing procedures was studied by Karchmer and Gunn [28] who revealed that unless care is taken, this method may lead to low results due to the stratification of the sample in the crucible, and the loss of volatiles such as lead and zinc halides, vanadyl and chromyl compounds. Although this procedure is still largely employed in industry, it is time consuming and could be unsafe because of the release of toxic vapours due to the low flash point of petroleum.

Alternatively, wet digestion of the oil samples ensures that the organic matrix is mineralized and the total metal content is converted to simple water soluble species. Wet digestion procedures for oil samples can be performed in closed or open vessels, using thermal energy or microwave radiation [29-32]. In the closed vessels, risk of contamination from airborne particulates is reduced, but in both cases, problems arise due to trace contamination from used digestion vessels and from the relatively large volume of mineralizing acids used (especially in the open vessel procedure). The risk of explosion still remains when using microwave digestion in closed vessels. Extraction with acids is an applicable procedure but not with heavy petroleum products containing high levels of asphaltenes, and for volatile gasoline that have very high vapour pressure [11,29]. Acid extraction using ultrasound-assisted digestion in which crude oil was treated with concentrated nitric acid and heated at 85 °C for 30 min has been proposed. The obtained mixture was placed in an ultrasonic bath for 15 min and then was aspirated directly into an ICP-OES instrument. Satisfactory recoveries were achieved for standard reference materials used to

validate the method [21,33].

Dilution of crude oil with organic solvents (*e.g.* MIBK, kerosene, xylene, ...*etc*) [11, 27,32,34,35] is by far the most studied and used direct introduction technique for ICP instruments [11,36], because it reduces sample preparation time, decreases analyte losses and reduces sample contamination [20]. However, other difficulties arise from the wide range of densities, viscosities, flammability and the increased care required for safe disposal. In addition, the increased solvent plasma load (SPL) is a critical problem that has been identified. The solvent load can cause instability and extinction of the plasma. Furthermore, the background levels due to carbon build-up [11] are increased necessitating the introduction of oxygen to the plasma to reduce molecular band emissions and prevent carbon build-up. Desolvation devices such as ultrasonic nebulizers (USN) [11,21,23] have been used to reduce the amount of solvent introduced into the plasma.

A multi-element optimization of the operating parameters for simultaneous ICP-OES with a charge injection device detector for the analysis of samples dissolved in organic solvents was carried out by Chirinos *et al.* [37]. They found that the nebulizer pressure is the factor that must be carefully optimized when using a volatile organic solvent.

Emulsification of the sample with surfactant agents and water forming oil-in-water emulsions is an alternative that offers the possibility of circumventing the problem identified above. This approach does not require the destruction of the organic matter or the use of large amounts of organic solvents. The use of emulsions can reduce the

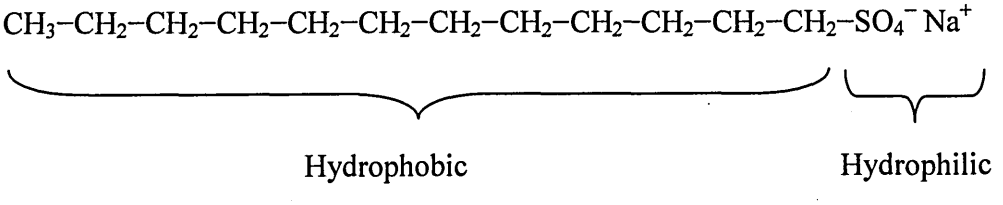
organic content of the sample solution down to 5% w/w. When the oil is evenly dispersed in the water phase, the sample behaves similarly to an aqueous solution.

1.7 Emulsion

An emulsion is a heterogeneous system of two liquid phases, one of which is dispersed as microdroplets throughout the other by mechanical agitation [38]. Since the resulting system has no or little stability, a surfactant is added to make the liquids more compatible and facilitates the emulsification and often promotes stabilization of the mixture [39].

Surfactants are usually organic compounds that are amphiphilic. That means; they contain both hydrophobic and hydrophilic groups. The head is the hydrophilic, water soluble part whilst the tail is the hydrophobic, water insoluble part . Since they are soluble in both organic solvents and water, they reduce the surface tension at the interface between the oil and water molecules and stabilize the emulsion.

The hydrophobic part of the surfactant is a hydrocarbon chain in either aliphatic or aromatic form or a mixture of both while the hydrophilic part is the part by which the surfactant is classified as anionic, cationic, nonionic or ampholytic which can behave as either anionic, cationic or nonionic [40]. An example of a surfactant is sodium dodecylsulphate (SDS):



Nonionic surfactants are the most commonly used in oil-in-water microemulsions because they are compatible with the other types of surfactant and their properties are little affected by pH.

The amphiphilic nature of the nonionic surfactant is expressed in terms of the balance between the hydrophilic and hydrophobic parts of the molecule (hydrophile-lipophile balance (HLB) number) and can be used to characterize the affinity of surfactants for aqueous and organic phases. A high HLB number generally indicates good surfactant solubility in water, while a low HLB number indicates a lower aqueous solubility and higher relative affinity for the organic phase [40].

The water soluble part of nonionic surfactants can be hydroxyl groups or polyoxyethylene chains. There are polyoxyethylated nonylphenols with a wide range of oxyethylene chain lengths from 1.5 to 100. Surfactants with low oxyethylene chain lengths are water insoluble and are water-in-oil emulsifying agents, while longer oxyethylene chain lengths are water soluble and produce oil-in-water emulsions.

Polyoxyethylated t-octylphenols are available as the Triton-X series which includes X-114 (E_{7-8}), X-100 (E_{9-10}) and X-102 (E_{12-13}). Surfactants with hydrophile-lipophile balance (HLB) values between 8 and 18 tend to form oil-in-water emulsions [24,41]. Therefore Triton X-100 (HLB = 13.5) has been successfully employed in the formation of emulsions in petroleum oils. Figure 3 shows surfactants surround water droplets and the polar–hydrophilic end is in the aqueous phase while the hydrophobic end is in the oil phase [42].

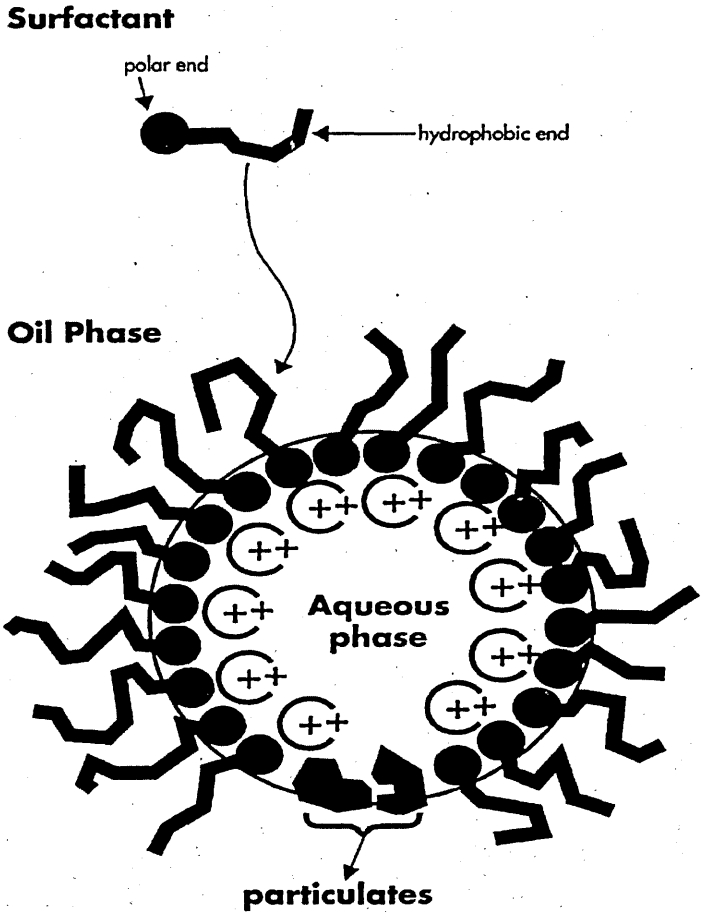


Figure. 3 Schematic for a water-in-oil emulsions. It shows a water droplet dispersed in oil with the hydrophilic end of the surfactant in the aqueous phase while the hydrophobic end is in the oil phase [42].

In the early eighties, Polo-Dies *et al.* [43] proposed a method for the determination of lead in gasoline by FAAS using an emulsion. They recommended mixing 1ml of gasoline with 20 ml of water and 5 drops of emulsifier with HLB 13.5 and shaking vigorously to form an emulsion which was then introduced directly into the flame. The results showed the applicability of the procedure and the sensitivity of the absorption signals was about 15 times higher than those from aqueous solutions. De la Guardia and Sanches [44] reported a method for the determination of manganese in gasoline by FAAS using an emulsion in which 10 ml of the sample was mixed with a sufficient amount of (1:1) Br_2-CCl_4 solution. After evaporation of the excess amount of bromine, 4ml of emulsogen and a small amount of water were added with stirring until a clear solution was obtained. This method gave good results when compared with a colorimetric method. However, care had to be taken because the reaction was exothermic. V, Ni, Fe, Mg and Na determination was investigated by Platteau and Carrillo [45] using FAAS. Highly stable crude oil emulsions were prepared by mixing 3g of homogenized crude oil, 15 ml of ethyl alcohol and 0.3g of linear alkylbenzene sulfonic acid (10 wt%). The homogenized mixture then was subject to a dry ashing procedure (ignition, burning in muffle furnace at 550 ± 5°C, dissolving the ash with acids). The method was shown to be reliable and accurate but at the same time it was time consuming. In addition, changes in V and Na signals due to the ionization effect for V in a nitrous oxide-acetylene flame and for Na in the air-acetylene flame required the addition of ionization suppressants. For Na, 2000 mg L^{-1} K was added to the standards and samples, while Al was used to suppress the ionization effect for V.

Aucélio and Curtius [17] determined the concentrations of As, Se and Sb in gasoline and kerosene by ETAAS using two sample preparation procedures. The first procedure involved the formation of a detergentless microemulsion by mixing an appropriate amount of the sample with water and propan-1-ol; (10:25:65) v/v/v for gasoline and (10:15:75) v/v/v for kerosene and 1 ml of concentrated nitric acid in a 10 ml volumetric flask. In the second procedure, a surfactant microemulsion was prepared in which 10 % of the sample was mixed with 1mL concentrated nitric acid and the mixture was sonicated for 5 min, then 4% v/v non-ionic surfactant (Triton X-100) was added. Mechanical agitation was used in both procedures. The preparation of oil samples as surfactant microemulsions were found to be the most appropriate, although they were stable for only 10 min. However, direct correlation between analyte signals in the sample and in an aqueous standard were found to be satisfactory.

Silva *et al.* [46] described a method for the determination of lead and copper in kerosene by ETAAS. A three- component solution was prepared from kerosene, propan-1-ol and 0.2 % nitric acid (5:11:2 ml respectively). This three component solution provided adequate stability (24 h) which made it possible to determine both elements in the presence of Pd as modifier. Burguera *et al.* [47] developed a procedure to form an on-line emulsification of lubricating oils to determine chromium by a flow injection system and ETAAS. The surfactant used for this study was sodium dodecylsulphate (SDS) with an HBL of 40.0 and hexane as co-solvent. It was considered that the addition of any modifier would bring no further advantage. The results were precise and the recovery values were between 99.2 to 102.2%.

Aucélio and Curtius [32] described the determination of silver by ETAAS in used lubricating oils. In a 10 ml volumetric flask, 0.2 g of the sample and 0.5 ml concentrated HNO_3 were mixed and sonicated for 5 min. A volume of 0.5 ml of xylene was added with 0.4 ml of Triton X-100. Water was added dropwise with continual agitation. In this study, a comparison was made of the three methods; dilution with organic solvent, acid digestion and the formation of emulsion. The latter was found to be the most effective, although it was stable for only 30 min. The same authors with Welz [48] applied the previous procedure to determine Sb and Sn in used lubricating oil by ETAAS with aqueous calibration. The accuracy and repeatability of the method was verified by using two standard reference materials (SRM 1084a and SRM 1085a). Ru was used as a modifier for both elements and results showed good correlation between absorbance signals for spiked emulsions and aqueous standards.

A three component system (gasoline-ethanol-water) was prepared by Ozcan and Akman [49] to determine Cu, Co and Pb in gasoline by ETAAS using an aqueous standard addition method. 1 ml of gasoline was mixed with 2.5 ml of water and 0.5 ml of concentrated HNO_3 followed by the addition of standard solution then completion to 10 ml with 96% ethanol. It was reported that the addition of nitric acid to the three component system is required in order to attain accurate determination of the analytes. Results were verified by microwave digestion using HNO_3, where it was found that there was no significant difference between the two methods. Matos Reyes and Campos [50] developed a method for the determination of Ni and Pb in diesel and gasoline samples stabilized as a microemulsion, using graphite furnace atomic

absorption spectrometry. Long term sample stabilization was obtained by mixing 3.3 ml of the sample with 6.5 ml propan-1-ol and 0.1 ml of 50 % v/v HNO_3. A transparent microemulsion was attained which was stable for more than 15 days. Aqueous modifiers such as Pd and Mg showed good performance for Pb measurement.

The determination of trace metals in lubricating oils using atomic spectrometric techniques has been reviewed by Aucélio *et al.* [51] highlighting problems related to sample pretreatment and calibration, as well as strategies to overcome them.

Aluminum was determined by Burguera *et al.* [52] in lubricating oils emulsified in a sequential injection analysis system by ETAAS. 0.5 ml of the sample was mixed with 1 ml of sec-butanol solution and 1 ml of the surfactant mixture then they were subjected to 5 sequences during which standard addition was used in order to study the matrix interference on the aluminum absorbance. No significant difference was found when compared with that obtained from a single calibration curve.

Inductively coupled plasma optical emission spectrometry has been used successfully for the determination of trace elements in crude oil and its derivatives. ICP-OES was used by Souza *et al.* [53] for the determination of Ni, Mo, Cr, V, and Ti in used lubricating oil. 0.2 ml of sample was acidified using 0.5 ml concentrated HNO_3 then emulsified by adding 0.5 ml xylene as co-solvent and 0.6 ml Triton X-100 as surfactant. An inorganic standard was used for calibration and three different certified lubricating oils were analyzed. Although the emulsion was stable for only 40 min, good accuracy was achieved for Ni, Mo, V and Ti while for Cr the recovery was slightly worse, however such behaviour for Cr is not unusual in oil samples

[53,55,56].

A procedure to prepare crude oil samples as detergentless microemulsions to determine Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr and Co by ICP-OES was demonstrated by Souza *et al.* [54]. The composition of the microemulsions was 0.6 g of crude oil (previously dissolved in 0.5 ml of xylene) mixed with 0.4 ml of concentrated nitric acid. Then propan-1-ol and water were added in an alternate way (1.1 ml of propan-1-ol followed by 0.25 ml of water) until a final mass of 10 g was attained. Oxygen was used in the nebulizer gas flow in order to minimize carbon building up and background. Standard reference material (SRM 1634c) was used to verify the accuracy of the method and the recoveries were between 97.9% and 103.8%. Souza *et al.* [55] also compared two sample emulsification procedures (Triton X-100 emulsion and detergentless emulsions) for the determination of Mo, Cr, V and Ti in diesel and fuel oil by ICP-OES. For detergentless emulsions, 2.5 g of the sample was acidified with 0.5 ml of concentrated nitric acid and mixed with 6 ml of propan-1-ol. Water was used as a complement of these compositions. For detergent emulsion, 1.5 g of the sample previously dissolved in xylene was placed in a 10 ml volumetric flask with 0.5 ml of concentrated nitric acid. The mixture was placed in an ultrasonic path for 5 min, then 0.3 ml of Triton X-100 was added followed by water. The whole compositions were sonicated for 5 min after vigorous shaking for 2 min. In the two cases (Triton X-100 emulsion and detergentless emulsions), milky homogeneous emulsions were achieved which separated shortly into two phases that could be readily reconstituted after manual shaking. Good recoveries and better results were obtained for detergent emulsions with concentrated nitric acid, with limits of

detection at the ng g^{-1} level. Oxygen was used as auxiliary gas flow to minimize carbon buildup and plasma background.

Not only crude oil and its derivatives were studied using the emulsification procedure but vegetable oils, margarine and butter were investigated as well by Souza *et al.* [56]. ICP-OES was used for determination of six elements (Cd, Co, Cr, Cu, Ni and Mn) in olive oil, soy oil, margarine and butter which were prepared using two procedures (detergent and detergentless emulsions). In order to prepare detergent emulsions in a 10 ml volumetric flask, 0.2 g of the sample, 0.5 ml of concentrated HNO_3 with an amount between 0.1 and 2 g of Triton X-100 were added. It was reported that the Triton X-100 emulsion for soy and olive oils gave very short stabilities (less than 3 min). While for margarine and butter, even when the samples were previously dissolved in 0.5 ml of xylene, Triton X-100 emulsions were not formed. The second procedure described by Souza involved the formation of detergentless emulsions by weighing an amount between 0.1 and 1 g of the sample into a 10 ml volumetric flask with 7 g of propan-1-ol and 0.5 ml of HNO_3. Margarine and butter were dissolved in 0.5 ml of xylene before any addition. After vigorous shaking the emulsions remained stable for a few hours. Good sensitivities with limits of detection in the ng g^{-1} range were achieved for the detergentless emulsions.

As some elements are found in the oil at very low concentration levels, inductively coupled plasma mass spectrometry could be a remarkable alternative, because of its high sensitivity and simultaneous detection that can be carried out easily and rapidly. A new approach for introducing crude oil directly into ICP-MS by forming a microemulsion using tetralin and Triton X-100 was described by Lord [24]. About

0.5 g of crude oil with an equivalent amount of tetralin were weighed in a tared 60-ml glass bottle and the contents were mixed until a homogeneous mixture was achieved. Then 1 g of Triton X-100 was added and the mixture was mechanically agitated until reaching homogeneity. De-ionized water was added gradually with continual agitation until a final mass of 50 g was attained. The author reported the formation of a very stable emulsion with no phase separation even after several months of storage. Accuracy was verified by analyzing two standard reference materials (NBS 1634b and NBS 1085), and the results obtained were in good agreement with the certified values.

Al-Swaidan [10] provided a new automated technique for trace elements analysis by sequential injection analysis / inductively coupled plasma-mass spectrometry using an emulsion of crude oil. 0.5 g of oil was mixed with 1.5 ml of tetralin, 0.5 ml of Triton X-100 and 5 ml of 40 % nitric acid with graduate addition of water until 50 ml of homogenized solution was obtained. The sequential injection system easily introduces the samples to the ICP-MS. This technique enabled good results for Pb and Ni, while low concentration for V was obtained due to its background.

Al-Swaidan [57] also studied the determination of vanadium and nickel in some Saudi Arabian crude oils and petroleum products (aviation turbine oil, gasoline and diesel fuel oil) by ICP-MS using the previous technique described by Lord [24] and the concentrations were measured using a standard addition method. Reasonable detection limits were obtained and the recoveries of added metals were between 98 - 103 %.

This technique was successfully applied on light fractions of crude oil as well. V, Co, Ni, As, Hg and Pb were determined in naphtha by ICP-MS using Triton X-100 to form an emulsion without the addition of a co-solvent. Kumar and Gangadharan [22] mixed 2 ml of naphtha with 1ml of 2.5 % solution of Triton X-100 in a capped 5 ml container, with stirring with a magnetic stirrer for 20 min. Immediately after emulsification the solution was introduced into the ICP-MS. The recovery for Ni and Pb was close to the added value, for V was 60% and almost no recovery was attained for Hg and As when adding aqueous standard solutions to the emulsion. They recommended not to use an aqueous standard for calibration for analyzing emulsified naphtha. Saint'Pierre *et al.* [38] treated gasoline with concentrated HNO_3 and Triton X-100 to form an emulsion to determine Cu, Mn, Ni, and Sn by electrothermal vaporization ETV ICP-MS. They used the procedure described by Aucélio and Curtius [17]. They reported that this emulsion was stable for only few minutes and they recommended pre-concentrating the emulsion by repeated pipetting and drying. Gasoline was emulsified using tetralin and Triton X-100 by Heilmann *et al.* [58] to determine sulphur by Isotope Dilution ICP-MS. They used the procedure described by Lord [24] and they reported that the use of transparent microemulsions is a necessary precondition for precise and accurate sulphur analysis in gasoline and related fuel samples. A satisfactory accuracy was obtained by analyzing two different certified gas oil reference materials using the proposed procedure and comparing the recovery with those obtained by microwave assisted digestion.

Castillo *et al.* [59] described a simple method for a semiquantitative simultaneous determination of various metals in olive oil using direct emulsion nebulization with

ICP-MS. Approximately 2 g of oil was mixed with 1.5 ml of Triton X-100 and stirred mechanically and the homogenized mixture had a final weight of 50 g. In order to get a stable emulsion, the addition of HNO_3 was not recommended. Results from spike and recovery experiments at the level of 100 and 200 ng mL^{-1} were 93 – 136 % for all elements (Ba, Cd, Co, Cr, Cu, Ge, Mn, Ni, Tl, Pb, U and V) except for Zr which was found to range between 73.8 – 76.2 % . The detection limits were found to be suitable for very low concentrations of metals in olive oil.

1.8 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

ICP-MS is a fast, precise and accurate multi-element analytical technique for the simultaneous determination of trace elements in liquid and solid samples. Nearly all the elements in the periodic table can be analyzed by ICP-MS. The analytical range extends from ppt (pg g^{-1}) to ppm (µg g^{-1}). ICP-MS consists of the following components:

sample introduction system, excitation source, ion transport system, mass separation device, detector and data processing (Figure 4).

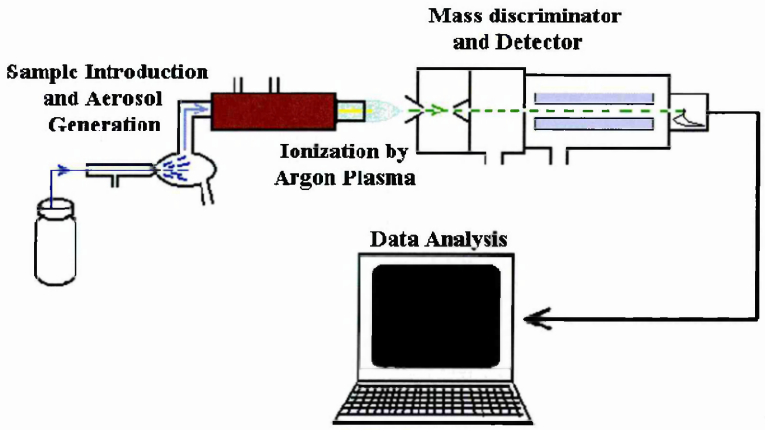


Figure. 4 Schematic of the main components and processes of an ICP-MS [60]

The samples are introduced into the plasma in the form of an aerosol by a nebulizer. There are a variety of nebulizers that can be used to produce such sample aerosols and the one used in this study was the Babington nebulizer. The nebulizer is connected to a spray chamber by which larger aerosol droplets are removed from the gas stream and the remaining smaller droplets are passed into the central channel of the argon plasma (Figure 5).

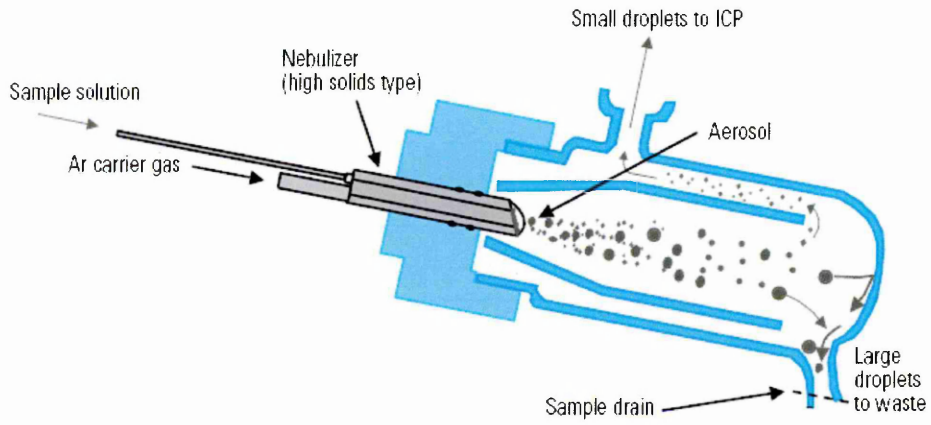


Figure. 5 Schematic diagram of an ICP-MS spray chamber [61]

The plasma is generated in a quartz torch, which consists of three concentric quartz tubes. The outer quartz tube introduces the auxiliary gas flow to the inner annular space. A flow of Ar gas carries the sample aerosol to the plasma through the central tube. The plasma is generated by applying a spark from a Tesla coil on the argon gas passing through the central tube of the quartz torch. The spark generates free electrons and ions which are coupled to the magnetic field formed as a result of the radio frequency current passing through the cooled copper coil placed around the torch (Figure 6). Temperatures in the plasma range from 6000 to 10,000 K. Once the aerosol droplets are introduced to the high temperature plasma, they are vaporized, atomized, then ionized [62].

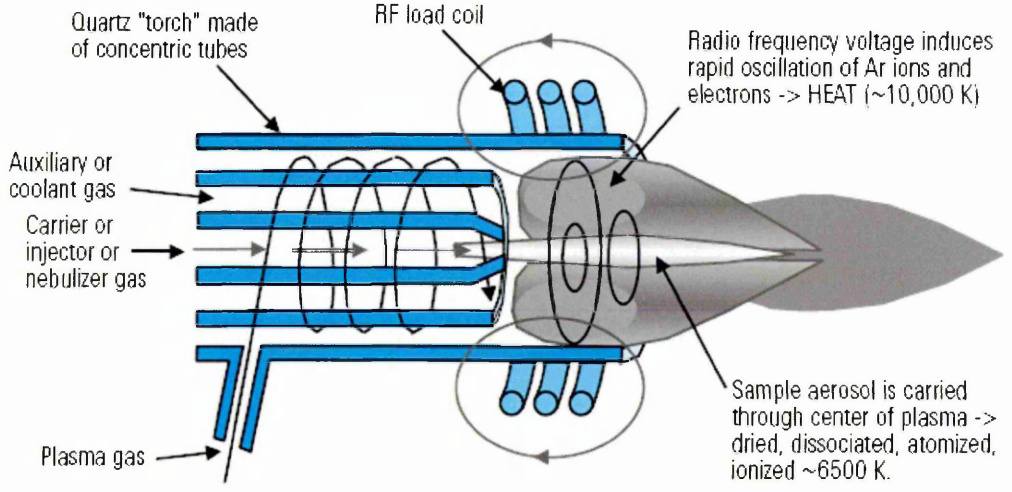


Figure. 6 ICP-MS plasma torch [61]

The produced ions are transferred to the mass spectrometer by an ion transport system that consists of the interface region and the ion lens system that perform the separation of the ions from the photons and residual neutral material. The ions in the centre of the plasma are sampled into the quadrupole mass spectrometer through the interface region that consists of two successive Ni cones with 1mm diameter. The first extraction of the ions is through the orifice of the sample cone into the region between the two cones where the pressure is about 1-3 torr by rotary vacuum pump. Further extraction for the ion beam is through the orifice of the skimmer cone into the ion lens system in the front part of the mass spectrometer where the pressure is about (10^{-3} - 10^{-4} torr) by turbo molecular vacuum pump. The positively charged ion lens extracts the positive ions from a matrix of neutral species and focuses the ion beam into the mass spectrometer (Figure 7).

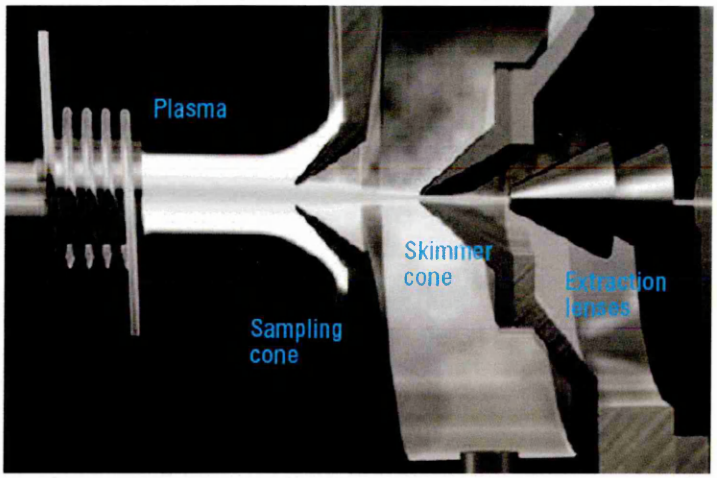


Figure. 7 Schematic of an ICP-MS sampling and skimmer cones with the extraction lenses [61]

The most commonly used mass separation device in ICP-MS is a quadrupole mass spectrometer which acts as a mass filter that separates ions according to their mass/charge ratio. The separated ions pass through the mass spectrometer to the detector to be measured. Ion signals are measured with an electron multiplier, which has its inside walls covered with a metal oxide. A negative voltage is applied to the multiplier to attract the positive ions. When the ions get in contact with the metal oxide wall they eject further electrons. These secondary electrons, which are accelerated down the tube by the potential gradient, hit another section of the coating and more secondary electrons are emitted. This process is repeated many times, so that in the end one ion collision leads to about 10^8 electrons. The multiplier can be operated in the pulse count or in the analogue mode depending on the concentration of the analytes being measured. In the pulse count mode the negative voltage applied is higher and more secondary electrons are produced. The electrons are detected as a single pulse. This mode is used for concentrations ranging from the detection limit up to 1 mg L^{-1}. The analogue mode (one ion collision leads to about 10^4 electrons) is suitable for concentrations between 1 and 100 mg L^{-1}. In this mode the multiplier does not become saturated. The ion intensity is converted to a pulse counting signal. The signal is measured as a current which is subsequently converted into counts per seconds (cps).

1.8.1 Instrument Optimization and Tuning

The stability of the signal intensity provided by ICP-MS instruments depends on the plasma operating conditions. Instrument optimization involves maximizing the signal-to-noise ratio (usually for the middle of the mass range isotope such as ^{103}Rh) by finding the optimal nebulizer gas flow rate, ion lens voltages and RF power. At the same time, care must be taken to minimize the production of doubly charged ions (increases with decreasing nebulizer gas flow and also depends on the position of the plasma relative to the interface cones) and of molecular ions such as oxides (decreases with decreasing nebulizer gas flow and also depends on the position of the plasma relative to the interface cones).

1.8.2 Interferences

A few interferences do occur in ICP-MS, but these are generally predictable and can often be corrected for or may be minimized by optimizing instrument operating conditions. Three types of interferences can occur in ICP-MS measurements:

1.8.2.1 Isobaric Interferences

They occur for equal mass isotopes of different elements (*e.g.* ^{58}Fe on ^{58}Ni ^{64}Ni on ^{64}Zn ^{48}Ca on ^{48}Ti) and these are best avoided by choosing alternative isotopes.

1.8.2.2 Molecular (or Polyatomic) Interferences

They occur due to the recombination of sample and matrix ions with Ar or other matrix components (*e.g.* O, N, Cl, ...*etc*) in the cooler region of the plasma.

(*e.g.* $^{40}Ar^{16}O$ on ^{56}Fe $^{47}Ti^{16}O$ on ^{63}Cu $^{40}Ar^{35}Cl$ on ^{75}As $^{40}Ar_2$ on ^{80}Se)

They can be avoided using alternative analyte isotopes or by applying correction factors determined by analyzing interference solutions. They can also be reduced or

eliminated by using more appropriate sample introduction systems such as ultrasonic nebulization (USN) and electrothermal vaporization (ETV) or optimizing instrument operating conditions.

1.8.2.3 Doubly- Charged Ion Interferences

They occur due to relatively rare doubly-charged matrix or sample ions with twice the mass of the analyte and hence the same mass/charge ratio (*e.g.* $^{90}Zr^{++}$ on $^{45}Sc^{+}$). It can generally be minimized by optimizing instrument operating conditions.

The volatile compounds are enriched in the aerosol/vapor stream that enters the plasma, due to their higher vapor pressure. The presence of those volatile organic compounds in a crude oil sample will cause signal enhancement thus increasing the polyatomic ion background [24]. The determination of some elements such as V, Cr and Fe by ICP-MS is known to suffer from the polyatomic isobaric interferences on ^{51}V caused by ^{34}S $^{16}OH^{+}$, on ^{56}Fe caused by ^{40}Ar $^{16}O^{+}$ and on ^{52}Cr caused by $^{40}Ar^{12}C^{+}$and $^{35}Cl^{16}O^{+}$ [63]. The deposited carbon on the cooler surfaces of the sample skimmer cone and ion lenses of ICP-MS, affects the transport efficiencies of ions and also carbon-argon species cause polyatomic interferences, which affect the determination of Mg, Cr and some other elements [23,64,65]. Table 2 depicts some important interferences in quadropole ICP-MS that are expected from organic crude oil matrices.

Table 2. Interferences from organic crude oil that may occur in quadrupole ICP-MS. Isotopic abundances quoted in brackets [23]

Measured Isotope %	Principle Interferences
^{27}Al (100)	$^{13}C^{14}N;^{12}C^{14}NH$
^{24}Mg (78.7);^{26}Mg (11.17)	$^{12}C^{12}C;^{13}C^{13}C$
^{44}Ca (2.06)	$^{12}C^{16}O^{16}O$
^{47}Ti (7.28)	$^{32}S^{17}O;^{36}Ar^{12}C$
^{52}Cr (83.79);^{53}Cr (9.55)	$^{40}Ar^{12}C;^{40}Ar^{13}C$
^{57}Fe (2.19)	$^{40}Ar^{17}O$
^{60}Ni (26.23); ^{62}Ni (3.66)	$^{36}Ar^{12}C^{12}C;^{36}Ar^{13}C^{13}C;^{38}Ar^{12}C^{12}C$
^{63}Cu (69.17);^{65}Cu (30.91)	$^{40}Ar^{23}Na;^{32}S^{33}S;^{32}S^{16}O^{17}O;^{32}S^{16}O_2H$
^{66}Zn (27.81)	$^{40}Ar^{13}C^{13}C;^{33}S^{33}S;^{34}S^{32}S$

1.8.3. Matrix Effects

Clogging of the orifices in either or both of the interface cones may be a problem when samples with high total dissolved solid (TDS) contents or oil samples are analyzed. The problem may be overcome by sample dilution or using an alternative sample introduction system (*e.g.* Ultrasonic nebulizer with a desolvation unit).

1.9 Reliable Measurements

1.9.1 Method Validation

Method Validation is the process of proving that an analytical method is acceptable for its anticipated purpose and it has a direct impact on the quality of the analytical data. In general, methods for regulatory submission most include studies on specificity, linearity, accuracy, precision, detection limit and quantification limit.

1.9.1.1 Specificity & selectivity

It is the ability of the method to accurately measure the analyte response in the presence of all potential sample components [66]. Therefore, in order to select a method for a particular analysis, we should take into consideration its ability to give accurate and precise results free of interferences and matrix effects especially in crude oil samples that contain high levels of organic compounds. For example, when selecting a method to analyze crude oil samples, there are some important points that should be focused on, such as: the volatiles content of the crude that may be lost during some steps in sample preparation techniques, the stability of the analytes of interest in the specimen solution and choosing the right technique that is most suitable to measure the concentration of the analytes in the sample accurately, precisely and with no interferences.

1.9.1.2 Accuracy or Bias

It is the closeness of the measured value to the true value for the sample. Accuracy is usually determined in one of four ways. First, accuracy can be assessed by analyzing a CRM and comparing the obtained result to the certified value. The second approach is to compare test results from the new method with results from an existing accurate

method. The third approach is a recovery study, which is performed by spiking analyte in blank matrices. The fourth approach is the standard addition technique, which can also be used to determine the recovery of spiked analyte

1.9.1.3 Precision

Precision is the closeness of the measured values to each other. An instrument precision study is performed by analyzing one sample solution 10 times to test the performance of the instrument by SD or RSD.

1.9.1.4 Limit of Detection (LOD)

It is the smallest concentration of analyte which can meaningfully be detected. It is also defined as $3*SD_o$ where SD_o is the standard deviation of the blank.

1.9.1.5 Limit of Quantification (LOQ)

It is the lowest amount of analyte in a sample which can be quantitatively determined. It is also defined as $10*SD_o$ where SD_o is the standard deviation of the blank.

1.10 Characterisation of Libyan Crude Oils

Giant oil fields were discovered in Libya from 1956 to 1961. Libya started exporting oil in 1961 and by 1966 it was the 7th largest oil-producing nation in the world. The extraordinary discoveries in the Sirt basin, where 19 of 21 giant fields were located with recoverable reserves of 40 billion barrels of oil (bbl) [67], attracted the international exploration companies all around the world to make further discoveries in Libya.

Aside from the Sirt basin, there are other onshore explorations, including areas in the Ghadames and Murzuq basins plus other explored areas such as Kufra (in the southeastern desert) and Crenaica-Botnan (near the Egyptian border) (Figure 8). Ghadames is Libya's second-most explored basin, and is linked geologically with oil and gas structures in Algeria and Tunisia. Murzuq has been a successful area for oil and gas exploration in recent years, with new fields including the El-Sharara and NC-174 (Elephant) fields [67].

There are also major discoveries in the Mediterranean at the north west of Libya where the offshore oil fields El- Bouri and Al-Jurf are found.

In this study, three Libyan crude oils were selected from different basins to determine the trace elements using microemulsion as a sample introduction technique into the plasma, for ICP-MS analysis. The characterizations of the selected oils are as follows:

a) El-Bouri oil field off Libya's western coast is the largest producing oil field at around 110,000 bbl/d, in the Mediterranean sea. Italy's Eni is the developer of the field, which was discovered in 1976 at a depth of 8,700 feet. It is paraffinic with API gravity of 26 and 1.8 % S content.

b) El-Sharara oil field is in the Murzuq basin, in the desert south of Tripoli, producing around 100,000 bbl/d of light sweet oil. Repsol is the developer of the field and it leads a European consortium, which consists of Austria's OMV and Total of France. The crude oil is paraffinic with API gravity of 41.5 and a low S content of 0.6 %.

c) Amna crude oil was supplied by National oil Corporation. It is paraffinic with API gravity of 36.7 and a low S content of 0.17 %.

Table 3, shows the main characterizations of El-Bouri, El-Sharara and Amna crude oils and Figure 8 shows the locations of main basins in Libya.

Table 3 Characteristics of Libyan Crude Oils [68,69]

Crude Oil	El- Bouri	El-Sharara	Amna
Specific Gravity at 15.6/15.6 °C	0.8986	0.8179	0.8412
Density at 15 °C	0.8981	0.8170	0.8374
API Gravity	26.0	41.5	36.7
Total Sulphur, wt%	1.8	0.6	0.17
Pour Point, °C	+ 6	<- 33	+ 24
Type	Paraffinic	Paraffinic	Paraffinic

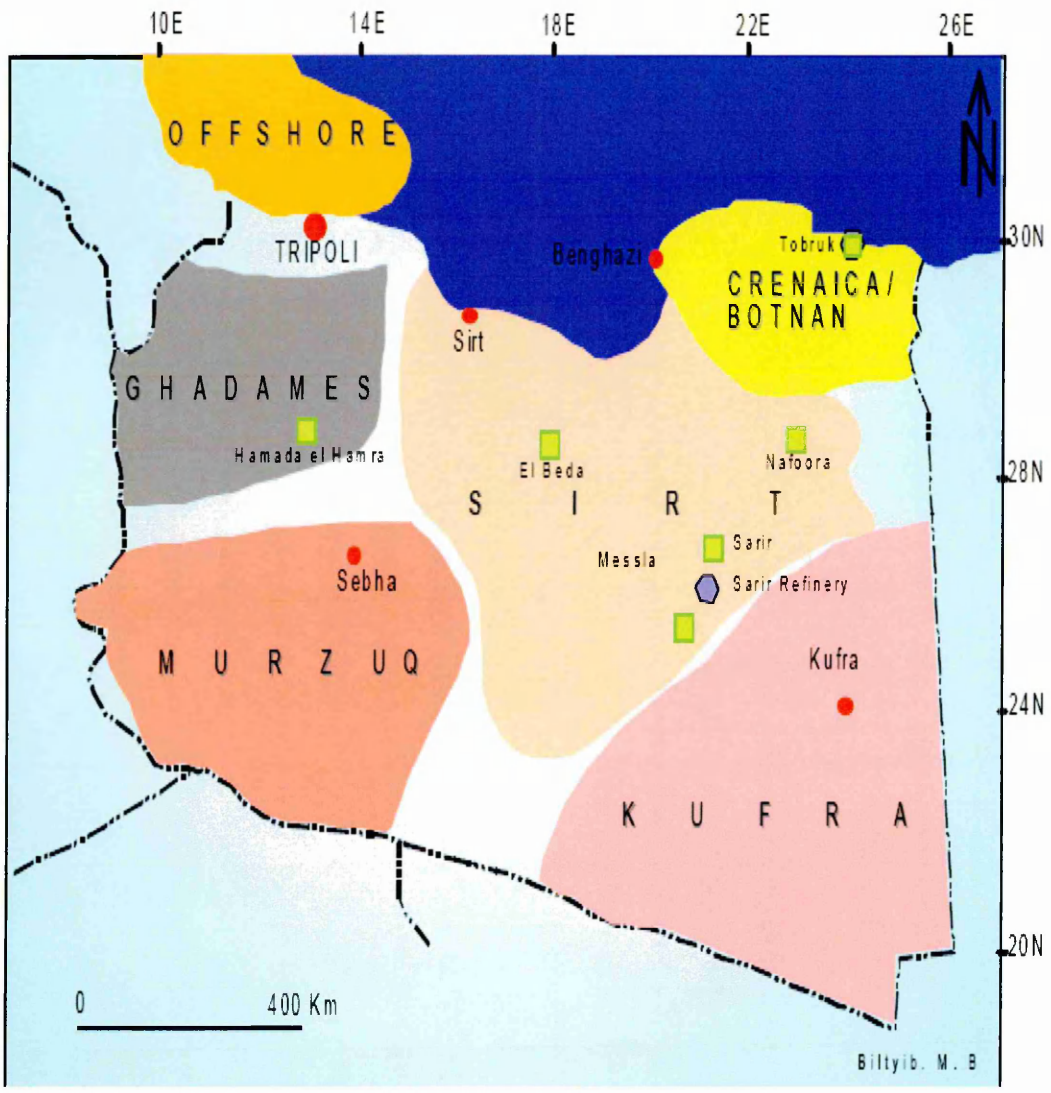


Figure. 8 The map of Libya with six sedimentary basins; Sirt, Ghadames, Murzuq, Kufra, Crenaica-Botnan and offshore Tripoli basin [70]

1.11 The approach adopted in the present study

1. The microemulsion formation was optimized and factors affecting the stability of the microemulsion were studied.

2. Calibration curves were established using emulsified multielement aqueous standards.

3. In order to validate the method, two certified reference materials; HU-1, (Used Oil) and NIST 1084a, (Wear Metals in Lubricating Oil) were emulsified and the obtained results were compared to other results from three different preparation methods (dry ash, wet digestion and microwave digestion).

4. A spike recovery test was made by spiking a significant amount of the standard solution to the emulsified samples which was then introduced to the plasma.

5. Analysis of two reference materials (HU-1, (Used Oil) and NIST 1084a, (Wear Metals in Lubricating Oil)) prepared with the proposed method in order to confirm the accuracy of the applied method.

6. A calibration using simple aqueous multielement standards was carried out.

7. Three Libyan crude oil samples were emulsified using the proposed methodology and introduced into the plasma in order to measure the trace elements (Ti, V, Ni, Cu, Mo, Mn, Cd, Sn and Pb) using ICP-MS.

8. A comparison was made between the results of the crude oil samples obtained using the microemulsion procedure to those obtained using dry ash, wet digestion and microwave digestion.

1.12 The Motivation

Demand from the petroleum industries for determination of trace metals such as Ni, V, Hg, As, and Pb in crude oil and its derivatives makes it very necessary to find an alternative, simple, rapid, and accurate sample preparation technique for simultaneous determination of trace metals. Those metals cause several problems in refinery processes because they poison catalysts and cause corrosion to the furnaces, and boilers, and consequently reduce the quality of petroleum products.

Introducing the crude oils directly to the plasma with out pre-treatment, leads to a variety of problems. However, wet digestion and dry ash procedures are time consuming and the sample may be exposed to contamination and there is the possibility of the loss of the analyte during the preparation steps. There is therefore, a need to develop an alternative sample preparation method. Emulsification of the crude oil has been shown to be a successful alternative technique.

1.13 The Aims

To develop an accurate and fast method for trace element determination in crude oils and to apply the method in routine analysis.

To allow access to the high sensitivity of ICP-MS for crude oil analysis without requiring acid decomposition of the crude oil samples.

To eliminate any potential loss of analyte elements due to volatilization or precipitation during the digestion procedures.

To reduce the time for sample preparation to a minimum.

To overcome the problem of carbon build-up on the mass spectrometer interface

To characterize selected Libyan crude oils quantitatively

Chapter 2

2. Experimental

2.1 Instrumentation

The spectrometer used in this study was a Hewlett Packard 4500 quadrupole inductively coupled plasma mass spectrometer (model number HP 4500 G1820A, manufactured in Japan) equipped with a Babington nebulizer. Argon 99.95% was used as the plasma gas. A peristaltic pump was used to feed the nebulization system with sample and standard solutions. A CE precision Ultrasonic Bath from England was used for microemulsion preparation. A ST Hotplate and a microwave digestion unit from CEM Corp. (USA) were used for acid dissolution of samples. The operating conditions are listed in Table 4.

Table 4 The operating conditions of HP Hewlett Packard 4500 ICP-MS

RF Power	1400 w	S/C Temp	2 °C
RF Matching	1.92 v	Integration Time	0.1 sec
Sample Depth	8 mm	Sampling Period	0.31 sec
Carrier Gas	1.22 L/min	Acquisition Time	22.83 sec
Blend Gas	0 L/min	Number of replicates	3
Peripump	0.1 rps	Calibration Mode	External Calibration
Nebulizer	Babington	Curve Fit	Linear
Auxiliary Gas Flow	1L/min	Carrier Gas Pressure	80 psi

2.2 Reagents

The water used in this study was ultra pure water obtained from an ELGA system, ultra ionic model, manufactured in UK. All glassware were soaked in 20% v/v nitric acid for several days and rinsed with hot nitric acid then with de-ionized water prior to use. Ti, V, Cr, Mn, Ni, Cu, Mo, Cd, Sn, and Pb standard solutions were prepared fresh from individual element stock standard solutions (1000 $\mu g\ ml^{-1}$) supplied by BDH Poole, England, and were used for calibration after specific serial dilution. Tetralin (1,2,3,4-tetrahydronaphthalene) supplied by Fluka AG was employed as the co-solvent. A non-ionic surfactant Triton X-100 98-100% (Isooctylphenoxy polyethoxy ethanol) supplied by BDH Poole, England was used as the emulsifying agent. Aristar grade nitric acid 69% Sp.g 1.42, sulphuric acid 95% Sp.g 1.84 and hydrogen peroxide 30% (supplied by BDH Poole, England) were used for this study. Analytical accuracy was evaluated by using certified reference material 1084a (wear metals in lubricating oils) supplied by NIST and HU-1 (used oil) supplied by SCP Science. Magnesium nitrate (supplied by BDH Poole, England) was used as an ashing aid in the dry ash procedure. Indium stock standard solution (1000 $\mu g\ ml^{-1}$) (supplied by BDH Poole, England) was used as an internal standard. Three Libyan crude oil samples (El-Bouri, El-Sharara and Amna) were supplied by the Libyan Petroleum Institute.

2.3 Sample Preparation

2.3.1 Dry Ashing

A 0.5 g aliquot of crude oil was weighed into a porcelain crucible and magnesium nitrate was added. The sample was burned and the residual carbon was then heated in a muffle furnace at 525 °C until a white ash was obtained. Then the inorganic residue is digested in dilute nitric acid. After filtration, the sample was made up to the volume (25 ml) with de-ionised water.

2.3.2 Wet Digestion

A 0.1 g aliquot of homogenized oil sample was weighed into a 100 ml beaker and 3 ml of sulphuric acid was added. The mixture was heated gently to avoid charring for about 15 minutes. Then 5 ml of nitric acid was added and the mixture boiled for 30 minutes after which the mixture was put aside to cool. 3 ml of hydrogen peroxide was added dropwise to the cold solution and the mixture boiled until a clear solution was obtained. The solution was filtered into a 100 ml flask and made up to the mark with de-ionised water [71].

2.3.3 Microwave Digestion

Amounts of 0.1 g of oil were placed in a Teflon bomb containing 2 ml of concentrated nitric acid. Samples were subjected four times to the following digestion program: 5 min at 300 W, 1 min at 0 W and 5 min at 600 W. The Teflon bombs were allowed to cool down (25 min) before each of the subsequent runs, and a new aliquot of 2 ml of concentrated HNO_3 (second and third runs) and 1 ml H_2O_2 (fourth run) was added to the vessel. The contents were then transferred to a 100 ml volumetric flask and diluted with de-ionised water [33].

2.3.4 Microemulsion Preparation

Oil-in-water microemulsions were prepared, as follows, using a specific sequence in order to guarantee its homogeneity: 0.1 g of a homogenous crude oil sample was weighed into a 100 ml clean and dry volumetric flask. An equivalent weight of Tetralin is added to the flask and the mixture was agitated mechanically using an ultrasonic bath for 7 min. 0.3 g of Triton X-100 is added to the solution and the mixture was mechanically agitated for 20 min at a temperature of 45 $^{\circ}$C to 55 $^{\circ}$C until a homogenous solution was obtained. 5 ml of de-ionized water was added dropwise with continual agitation, then the solution was made up to the mark with 0.1 % HNO_3 after adding In as an internal standard to get a final concentration of 20 ng ml^{-1} in the blank, standard and sample solutions. It is noteworthy that the order in which the components were mixed together is critical for successful microemulsion formation.

Chapter 3

3. Results and Discussion

One of the most important features of an atomic spectrometric analysis is, the development of an appropriate sample preparation procedure, which must be simple and able to convert the sample to a form compatible with the sample introduction system and atomizer. The other goal in choosing the sample preparation procedure is to minimize interferences on the analyte signal.

Crude oil and its derivatives are, in general, difficult to analyze because they have a high organic load and are viscous. Several procedures have been applied for this kind of sample. One of the most frequently used is emulsification of the sample using surfactants (detergent emulsions). Emulsification has been successfully applied to oils because the procedure decreases the organic load and therefore reduces the interferences due to the viscosity of the samples and the emulsified oil samples are compatible with sample introduction into the plasma.

3.1 Optimization of the Microemulsion Formation

The optimization of the ratio between oil and surfactant in order to form a microemulsion with good and long term stability was investigated. About 0.1% w/v sample was used in order to decrease the amount of oil introduced to the plasma and to avoid problems associated with polyatomic interferences and the matrix effect. This amount of oil was dissolved in an equivalent amount of tetralin, the co-solvent, prior to any further treatment. Tetralin was preferred to other organic solvents such as

xylene, because an emulsion with a lower vapour pressure was produced. The presence of volatile organic compounds can increase the level of polyatomic ion background. Lord [24] studied the effect of volatility by comparing the background spectra for microemulsions containing 1 % (w/w) either xylene or tetralin as co-solvents individually. He found that the high vapour pressure of crude oils caused enhancement of the polyatomic ion background and the resultant volatile compounds were enriched in the aerosol (vapour pressure) that entered the plasma affecting its temperature distributions and the abundance of analyte ions. He also found that the vapour pressure of the xylene was about 16 times higher than when using tetralin.

In this study, Triton X-100 was chosen as the surfactant because it is readily available in most laboratories. In addition, Triton X-100 (non-ionic surfactant) compared to the other surfactants such as anionic ones (eg. sodium dodecylsulphate), does not introduce cations such as sodium which gives rise to high background radiation in the plasma. Besides, anionic surfactants require an alkaline pH in order to stabilise aqueous solutions [24].

It has been reported that the mean droplet size of the emulsion depends on the surfactant type and concentration [72]. Therefore, the stability of the formed microemulsion increases with surfactant concentration [73], although at low and high surfactant concentrations microemulsions were unstable. The instability at high concentration of the surfactant could be due to the formation of large droplets [74]. Thus, in the proposed methodology, the investigated amount of surfactant (Triton X-100) was varied between 0.1 - 0.4 % w/v. The resultant microemulsion was inspected visually in terms of homogeneity, stability and appearance. The solution containing

0.1 % w/v surfactant was found to be unstable, quickly separating into the constituent phases. Microemulsions formed with 0.2 % w/v and 0.4 % w/v of the surfactant showed better homogeneity but rapid separation into two phases was observed and visible oil droplets were clearly seen. It was found that the optimal value of the surfactant was 0.3 % w/v.

The formed emulsion exhibited good homogeneity, with no noticeable oil droplets, and was stable for more than three months.

3.2 Factors Affecting Microemulsion Stability

In addition to the concentration of the surfactant, which was found to be critical for stability of the microemulsion, other factors were found to be important. These included sonication and temperature, acidity and dryness of the glassware.

3.2.1 Sonication and Temperature

Sonication and temperature are essential for the formation of a homogeneous transparent microemulsion with a small emulsion droplet size (EDS) that is stable for a long time. It has been demonstrated that the application of ultrasound can result in the formation of microemulsions with very small EDS. Sonication causes droplet deformation and disruption, and as a result EDS decreases [75]. Accordingly, many emulsion properties such as stability and colour depend on the EDS and size distributions. Lord [24] reported that the droplet size of the prepared microemulsion which exhibited stability that lasted for several months was between 10 to 60 nm. The importance of using temperature in forming good microemulsion has been described

in the literature [75,76]. It was concluded that temperature reduces the emulsion viscosity and interfacial tension, facilitating droplet break-up.

In this study, both temperature along with sonication were found to strongly affect the stability of the emulsions. The temperature required to form a good microemulsion was found to range between 45°C to 55°C. At these temperatures, the viscosity of the oil decreases enabling good homogeneity with the co-solvent and the Triton X-100. In addition, the micoemulsion exhibits good stability, even after cooling, which ensures that reliable results are obtained for the measured elements.

In order to demonstrate the influence of temperature and sonication on the homogeneity of the microemulsion and confirm whether reliable results can be obtained using this sample preparation method, CRM HU-1 used oil was emulsified using the proposed procedure with and without heat and sonication. Results in Table 5 show that those two factors can affect the accuracy of the results. Results for nickel was 45.5 $\mu g\ g^{-1}$ with heating and sonication and 37.4 $\mu g\ g^{-1}$ without. Cr, Mn and Pb results were also found to be higher at 12.7, 18, 20 $\mu g\ g^{-1}$ with sonication and heating, compared with 8.1, 15.1, 17.9 $\mu g\ g^{-1}$ respectively without sonication and heating. In contrast, the results of Ti, V and Cd were not affected.

Table 5. Used oil HU-1 trace elements concentration A) after forming a microemulsion with the use of temperature and sonication and B) after forming a microemulsion without the use of temperature and sonication.

Elements	A Used oil HU-1 $\mu g\ g^{-1}$	B Used oil HU-1 $\mu g\ g^{-1}$	Certified values $\mu g\ g^{-1}$
Ti	10.7 ± 1.5	9.5 ± 0.3	9 ± 2
V	7.5 ± 0.6	6.7 ± 0.3	7 ± 0.5
Cr	12.7± 6.8	8.1 ± 6.2	15 ± 2
Mn	18.0 ± 1.4	15.1 ± 0.4	18 ± 1
Ni	45.5 ± 3.7	37.4 ± 1.3	45 ± 3
Cd	15.7 ± 1.5	14.0 ± 0.2	15 ± 1
Pb	20.1 ± 1.9	17.9 ± 0.3	20 ± 1

3.2.2 Acidity (pH)

Acidification of the emulsion with strong inorganic acids allows the use of inorganic aqueous standards for calibration. It has been reported that the use of acidified emulsions enables a direct correlation between the signal of the analyte in the oil and the signal of analyte in aqueous standards [18]. Acidification of the microemulsion was used to convert metallic solid particles as well as metallorganic or oxide analyte species into dissolved inorganic analyte species. Such conversion improves the stability of the analytes in the sample, while minimizing the possibility of precipitation or adsorption of analyte species onto the sample container walls [51,55]. Poteau *et al* [77] investigated the influence of pH values (2, 4, 6, 8, 11, 12) on the stability of oil-in-water emulsions, and they reported that the emulsion is much more

stable at either pH 2 or 12, with the latter preferred, because asphaltenes contain more acidic groups than basic groups. Figure 9 published by Poteau *et al* [77] shows a picture of 6 emulsions prepared at different pH values ranging from 2 to 12 and it can be seen that the emulsion is more stable at pH = 2 and pH = 12 . Thiem and Watson [78] investigated the extraction efficiencies of emulsions for 21 elements in oil and transmission fluids by ICP-OES using different acids; HCl, HNO_3, H_2SO_4, and a (75:25) mixture of HCl and HNO_3. They found that both HCl and HNO_3 have good extraction efficiency with the recommendation to use HNO_3 if Ag and Pb were among the elements of interest.

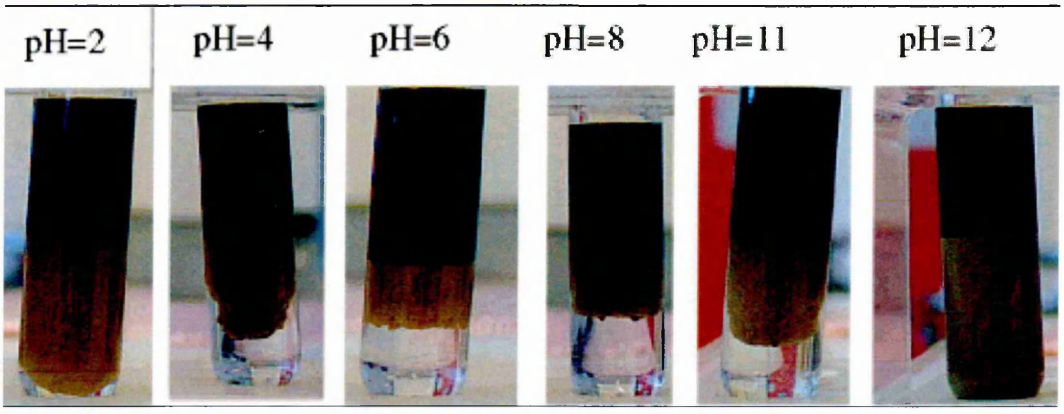


Figure. 9 Pictures of the emulsions formed after centrifugation for 30 min at pH between 2 and 12 [77].

The pH for the prepared microemulsion used in this study was 2.4 and it was found to provide good stability, which lasted more than three months without phase separation. In order to verify the significance of acidifying the microemulsion prior to introducing it into the plasma, El-Bouri, El-Sharara and Amna crude oil samples were emulsified using the proposed procedure with and without the addition of 0.1 % v/v nitric acid. From the visual inspection of the samples, the acidified microemulsions were clear, transparent, homogeneous and stable while the non-acidified microemulsion was cloudy and unclear. Figure 10 shows a picture for the emulsified crude oils (a) El-Sharara, (b) El-Bouri and (c) Amna prepared with the proposed method.

It is noticeable in Table 6 that the vanadium results for the El-Bouri, El-Sharara and Amna oil samples have increased from 22.2, 0.79, 0.6 $\mu g\ g^{-1}$ in the acidified microemulsion to 51.8, 1.4, 1.2 $\mu g\ g^{-1}$ in the non-acidified microemulsion, respectively. The nickel results were 20.0, <0.1, 2.1 $\mu g\ g^{-1}$ in the acidified microemulsion then increased to 48.4, 1.1, 7.1 $\mu g\ g^{-1}$ in the non-acidified microemulsion. This behaviour was similar to that observed for vanadium. This increase may be due to the polyatomic isobaric interference on ^{51}V caused by $^{34}S^{16}OH^{+}$ [20,63]. Interferences on Ni may be caused by $^{36}Ar^{12}C^{12}C$;$^{36}Ar^{13}C^{13}C$;$^{38}Ar^{12}C^{12}C$ [23]. For Ti, Mn, Cu, Sn Mo and Pb measurements, this trend was not observed.

Table 6 El-Bouri, El-Sharara and Amna crude oils microemulsion results with and without 0.1 % HNO_3 A and B, respectively. The results are in $\mu g\ g^{-1}$; for emulsified samples without acid (n=5) and for emulsified samples with the use of acid (n=5).

Element	Sample	Wet digestion $\mu g\ g^{-1}$	Microwave digestion $\mu g\ g^{-1}$	Microemulsion A $\mu g\ g^{-1}$	Microemulsion B $\mu g\ g^{-1}$
V	El-Bouri	22.4 ± 1.8	22.0 ± 0.8	22.2 ± 1.1	51.8 ± 8.4
	El-Sharara	0.5 ± 0.1	0.5 ± 0.02	0.79 ± 0.07	1.4 ± 0.2
	Amna	0.24 ± 0.08	0.25 ± 0.01	0.60 ± 0.02	1.2 ± 0.2
Ni	El-Bouri	23.8 ± 1.8	19.8 ± 1.0	20.0 ±1.4	48.4 ± 8.5
	El-Sharara	< 0.05	0.6 ± 0.2	< 0.1	1.1 ± 0.1
	Amna	2.8 ± 0.07	2.7 ± 0.4	2.1 ± 0.1	7.1 ± 0.5

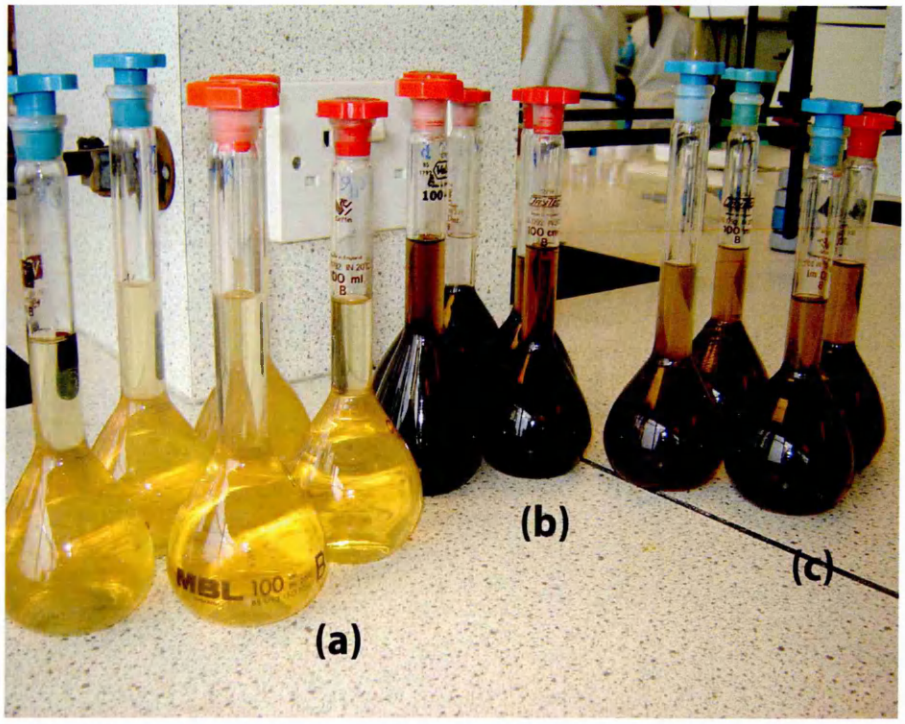


Figure. 10 A picture for the emulsified crude oils prepared with the proposed method. (a) El-Sharara, (b) El-Bouri and (c) Amna

3.2.3 Dryness of Glassware and Order of Addition of Emulsion Constituents

During this study, it was found that preparing the samples in wet glassware resulted in an unstable emulsion. In addition, the order in which the constituents of the emulsion were added together has been found to be critical [24]. Consequently the following procedure was developed: A small portion of oil is weighed in a clean dry flask followed by an equivalent amount of co-solvent (Tetralin) with mechanical agitation to homogenize the crude oil. Then an appropriate amount of surfactant (Triton X-100) is added with a continuous agitation. After that a small amount of de-ionized water (approximately 5 ml) is added dropwise with continuous agitation, then the flask is filled up to the mark with 0.1 % HNO_3 to obtain a clear transparent stable solution. Figure 11 shows a microemulsion prepared from Amna crude oil using the proposed method. It can be seen that the microemulsion is clear, transparent, homogeneous and stable. It does not contain any undissolved particles. In contrast, Figure. 12 shows the same crude prepared with the proposed procedure but without the use of heating, ultrasonic radiation, and the adding of nitric acid. The resulting solution was unclear and unstable, and after about 5 hours, it separated into distinct phases (Figure. 13).

Figure. 11 A stable transparent microemulsion of Amna crude oil prepared with the proposed method **:** 0.1% w/v of oil was mixed with 0.1% w/v tetralin with mechanical agitation using the ultrasonic bath at temperature between 45°C to 55°C , then 0.3% w/v Triton X-100 is added with a continuous agitation. After that, 5 ml of de-ionized water was added drop by drop with a continuous agitation then the flask was filled up to the mark with 0.1 % HNO_3.

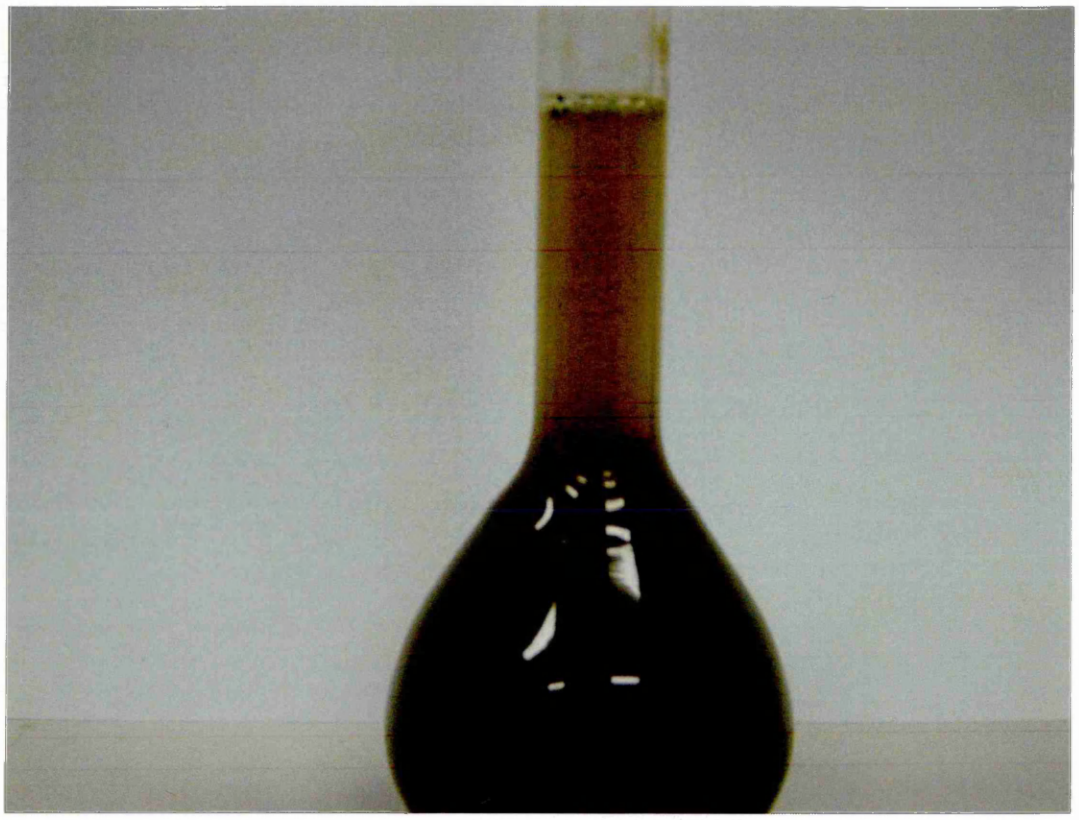


Figure. 12 An unstable unclear microemulsion of Amna crude oil prepared with the proposed method without the addition of acid and sonication.

Figure. 13 Separate phases of Amna crude oil microemulsion prepared with the proposed method without the addition of acid and sonication.

3.3 Analytical Figure of Merit

In this study, calibration curves were established using microemulsions containing increasing concentrations of inorganic standards 0.1, 1, 10, 100 μg L^{-1}, and In 20 μg L^{-1} as an internal standard added to both standard solutions and samples.

A blank was prepared in the same manner with the addition of 20 μg L^{-1} of In.

Good linearity for all ten elements was observed. Limits of detection (LOD) and limits of quantification (LOQ) were calculated using 3 times standard deviation of ten measurements of blank and 10 times standard deviation of ten measurements of blank, respectively. LOD was between 0.1 ng g^{-1} and 0.7 ng g^{-1} for all elements, and 4.8 ng g^{-1} for Cr. LOQ was between 0.2 ng g^{-1} and 2.4 ng g^{-1} for all elements, and 16.1 ng g^{-1} for Cr. The relative standard deviation was < 5% for all elements and 30.9% for Cr. The correlation coefficient (r^2) was 1.000 for all elements as can be seen in Table 7. Comparing LOD for Mn, Ni, Cu and Sn with those obtained by ETV-ICP-MS [38] (results displayed in Table 8) shows that they are very similar with a slightly higher Sn detection limit obtained by ICP-MS using the proposed method.

Table 7. Precision (RSDs), LODs, LOQs (ng g^{-1}) and (r^2) for trace elements determination using oil in water microemulsion by ICP-MS; number of replicates =10

Element	LOD ng g^{-1}	LOQ ng g^{-1}	RSD %	r^2
^{47}Ti	0.7	2.4	4.8	1.000
^{51}V	0.1	0.5	3.3	1.000
^{53}Cr	4.8	16.1	30.9	1.000
^{55}Mn	0.1	0.2	2.1	1.000
^{60}Ni	0.1	0.4	3.4	1.000
^{65}Cu	0.2	0.6	4.8	1.000
^{95}Mo	0.1	0.3	2.1	1.000
^{111}Cd	0.1	0.5	1.6	1.000
^{118}Sn	0.6	2.1	3.4	1.000
^{208}Pb	0.1	0.3	1.5	1.000

Table 8. Figures of merit for trace elements determination using oil in water emulsion by ETV-ICP-MS [38].

Element	r^2	LOD (µg L^{-1})
^{63}Cu	0.9979	0.22
^{55}Mn	0.9996	0.02
^{60}Ni	0.9966	0.38
^{120}Sn	0.9991	0.03

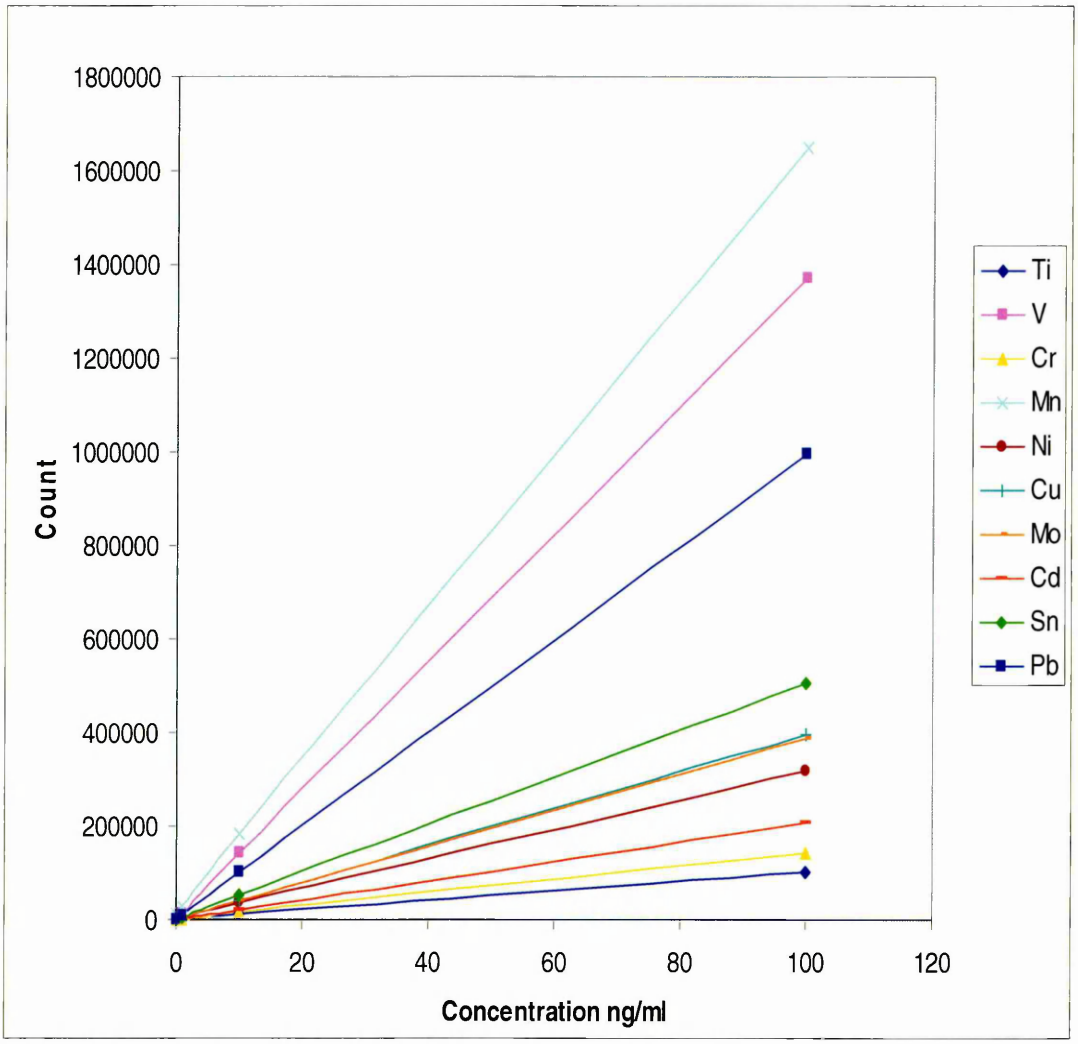


Figure. 14 Calibration curves for Ti, V, Cr, Ni, Cu, Mo, Mn, Cd, Sn and Pb microemulsion standard solutions analysed using ICP-MS. Refer to the relative standard deviation in Table 7.

3.4 Method Validation

The method was validated by comparing the obtained results for two certified reference materials; HU-1, (Used Oil) and NIST 1084a, (Wear Metals in Lubricating Oil) prepared using the emulsification procedure with those obtained using three different preparation methods; wet digestion, dry ash and microwave digestion. The results obtained for HU-1 used oil and NIST 1084a are given in Tables 9&10, respectively and comparison of the results shown in both tables indicates that there is a very good agreement between the four methods.

Table 9, generally shows a very good agreement between the results of the four procedures with excellent performance for all elements when the microemulsion method was used. A decrease in performance is seen for Cr may be due to the increased background signal caused by the organic matter. The decrease in Ni, Mo, Cd and Pb results with the dry ash procedure may have been due to the volatility of the compounds of those elements during the ashing step.

A statistical F-Test was applied on the results of Table 9 (comparing microemulsion with wet digestion, dry ash and microwave digestion, respectively) and it was found that the calculated F values were 1.02, 1.29 and 1.36 which were less than the F value from the table $F_{5,4}(0.05) = 6.26$. The results proved that the variances between the results are likely to be the same. An unpaired t-Test was also performed and the calculated t values were – 0.04, 0.05 and 0.036 which were less than t_7 from tables $t_7(0.01,0.025,0.05)= 2.998, 2.365, 1.895$ which means that there was no significant difference between the results. F-Test was also applied on the results of Table 10 (comparing microemulsion with wet digestion, dry ash and microwave digestion,

respectively) and it was found that the calculated F values were 0.12, 1.18 and 2.37 which were less than the F value from the table $F_{5,4}(0.05) = 6.26$. The results proved that the variances between the results are likely to be similar. An unpaired t-Test was also performed and the calculated t values were -0.24, 0.033 and 0.007 which were less than t_7 from tables $t_7(0.01,0.025,0.05)= 2.998, 2.365, 1.895$ which confirmed that there was no significant difference between the results [81].

Table 9 Comparison of HU-1 Used Oil analytes results prepared with the proposed methodology and traditional sample preparation methods with the certified values ± standard deviation.(n=5)

Element	Wet Digestion $\mu g\ g^{-1}$	Dry Ash $\mu g\ g^{-1}$	Microemulsion $\mu g\ g^{-1}$	Microwave $\mu g\ g^{-1}$	Certified values $\mu g\ g^{-1}$
Ti	15.6 ± 2.8	13 ± 1.1	10.7 ± 1.5	12.5 ± 0.6	9 ± 2
V	7.5 ± 0.4	6.9 ± 0.6	7.5 ± 0.6	7.1 ± 0.4	7 ± 0.5
Cr	17.2 ± 1.1	15.5 ± 1.4	12.7± 6.8	15.2 ± 0.7	15 ± 2
Mn	20.1 ± 1.4	17.1 ± 0.3	18.0 ± 1.4	16.5 ± 2.0	18 ± 1
Ni	46.9 ± 0.9	40.3 ± 3.6	45.5 ± 3.7	40.2 ± 2.1	45 ± 3
Mo	11.5 ± 0.4	9.5 ± 0.9	12.4 ± 0.9	10.4 ± 0.6	11 ± 1
Cd	12.4 ± 0.6	9.8 ± 0.8	15.7 ± 1.5	12.4 ± 0.7	15 ± 1
Pb	22.2 ± 1.6	16.3 ± 1.1	20.1 ± 1.9	17.6 ± 1.0	20 ± 1

As shown in Table 10, the results obtained for Ti, V, Ni, Cu and Mo in the1084a CRM are in good agreement using the four methods, and also with the certified values. Low Cr measured values have been reported by others [53,55,56]. The low result was attributed to the increased background signal caused by the organic matter [53]. Both the emulsification and dry ash procedure results were lower than those obtained by wet and microwave digestion procedures.

The results show that emulsion formation can be successfully applied to the determination of trace elements in crude oil. The results are reliable and sample preparation is less time consuming.

Table 10 Comparing NIST 1084a Wear-Metals in Lubricating Oil analytes results prepared with the proposed methodology and traditional sample preparation methods with the certified values ± standard deviation.

Element	Wet Digestion $\mu g\ g^{-1}$	Dry Ash $\mu g\ g^{-1}$	Emulsion $\mu g\ g^{-1}$	Microwave $\mu g\ g^{-1}$	Certified values $\mu g\ g^{-1}$
Ti	96.9 ± 2.5	101.8 ± 2.5	95.4 ± 1.8	95.0 ± 2.0	100.4 ± 3.8
V	97.4 ± 1.4	95.8 ± 1.9	95.2 ± 1.8	97.3 ± 3.1	95.9 ± 9.4
Cr	96.2 ± 0.3	90.5 ± 1.2	77.7 ± 4.1	89.6 ± 2.6	98.3 ± 0.8
Ni	99 ± 0.7	92.8 ± 2.1	99.8 ± 1.9	97.4 ± 3.4	99.7 ± 1.6
Cu	99.2 ± 2.1	96.8 ± 2.8	99.4 ± 1.5	93.7 ± 2.7	100.0 ± 1.9
Mo	104.2 ± 1.6	94.1 ± 3.8	94.9 ± 3.0	92.0 ± 2.5	100.3 ± 1.4
Sn	98.1 ± 0.2	81.8 ± 0.9	94.2 ± 2.6	82.6 ± 2.5	97.2 ± 2.6
Pb	96 ± 2.8	82.9 ± 2.5	85.8 ± 8.6	93.8 ± 2.0	101.1 ± 1.3

3.5 Recovery Test

In order to evaluate the accuracy of the method, a spike recovery test was performed on the Elsharara crude oil (Figure 15). Multielement standards were used to spike the samples so that the emulsion solutions contained 2 and 10 $\mu g\ L^{-1}$ respectively. Table 11, shows the good recovery of the 2 $\mu g\ L^{-1}$ spike, ranging from 95% to 120% for all elements, while Mo and Sn recoveries were 83.4% and 77.8% respectively. The recovery was improved for the 10 $\mu g\ L^{-1}$ spike, ranging from 93.3% to 101.0 % with relative standard deviation less than 5% for all elements except for Cr, where the result was higher in the two spikes. This behaviour has been observed before [53,55,56] without a possible explanation. Despite the variable results across the study, the determination of Cr is not crucial in oil samples. This demonstrates that the method developed here is appropriate for oil samples but possibly not for other kind of samples where Cr is important.

Figure. 15. Emulsified El-Sharara Libyan crude oil samples spiked with 10 $\mu g\ L^{-1}$ of a multielement standard solution.

Table 11 Analyte recovery in El-Sharara oil sample spiked with 2 and 10 μg L^{-1} standards. (n= 5)

Element	Spike concn: 2 μg L^{-1}			Spike concn: 10 μg L^{-1}		
	Mean	Recovery %	RSD %	Mean	Recovery %	RSD %
Ti	2.4	120.0	26.5	10.0	100.3	4.8
V	2.1	106.0	1.6	10.0	100.0	3.3
Cr	3.8	194.0	21.6	15.1	151.1	30.9
Mn	2.2	110.2	1.3	10.0	100.2	2.1
Ni	2.0	98.1	33.0	9.6	96.3	3.4
Cu	2.1	103.3	16.3	9.7	97.3	4.8
Mo	1.7	83.4	2.5	9.5	95.2	2.1
Cd	1.9	95.8	13.0	9.9	99.3	1.6
Sn	1.6	77.8	3.8	9.3	93.3	3.4
Pb	2.1	103.9	8.9	10.1	101.0	1.5

The excellent results obtained from the spike recovery test indicate that the proposed procedure can be applied to the determination of low element concentrations in crude oil without the risk of interference or analyte transport associated problems or high background.

3.6 Analysis of Reference Materials

The accuracy of the method was evaluated by the analysis of two standard reference materials HU-1 used oil and NIST SRM 1084a using the emulsification procedure.

Table 12 shows the good recovery for the eight elements determined in emulsified HU-1 used oil. Apart from chromium, the recoveries for the rest of the elements ranged from 100.1 % to 119.9 % . The chromium recovery was 85.1 % . This decrease may be due to the increased background signal caused by the organic matter. As shown in Table 13, good recovery (between 94.7% and 100.1 %) for eight elements of NIST 1084a were obtained. Excellent agreement with the certified results was obtained for Ni, V, and Cu. There was a slight decrease in Cr and Pb recovery, 79.1% and 84.8 %, respectively. Such behaviour for Cr in crude oils was also reported by other authors [53,55,56]. A statistical t-test was applied (comparing the measured and certified values for HU-1 used oil) and it was found that the calculated t values for all elements in Table 12 is less than t_5 from tables (0.01) = 3.365 and in Table 13 (comparing the measured and certified values for NIST SRM 1084a) is less than t_3 from tables (0.01) = 4.541. Consequently, there was no significant difference between the measured and certified results at $\alpha = 0.01$ [81]. Cr and Ti calculated t values for 1084a CRM were slightly higher.

The results achieved for the analysis of both CRMs, confirm the accuracy of the proposed method for both low and high element concentrations, especially for vanadium, nickel and copper measurements in oil samples along with satisfactory results for other elements. The method developed is suitable for routine application

because sample preparation is less time consuming and does not require prior removal of the hydrocarbons before sample analysis.

Table 12 The analysis of the HU-1 Used Oil with the proposed method ± standard deviation (n=6). t_5 from tables (0.01) = 3.365

Element	Measured value $\mu g\ g^{-1}$	Certified value $\mu g\ g^{-1}$	Recovery %	Calculated *t* value
Ti	10.7 ± 1.5	9 ± 2	119.9	2.9
V	7.5 ± 0.6	7 ± 0.5	107.2	1.9
Cr	12.7± 6.8	15 ± 2	85.1	-0.7
Mn	18.0 ± 1.4	18 ± 1	100.1	0.0
Ni	45.5 ± 3.7	45 ± 3	101.2	0.3
Mo	12.4 ± 0.9	11 ± 1	112.7	3.1
Cd	15.7 ± 1.5	15 ± 1	105.1	1.1
Pb	20.1 ± 1.9	20 ± 1	100.9	0.2

Table 13 The analysis of the NIST 1084a Wear-Metals in Lubricating Oil with the proposed method ± standard deviation (n=4). t_3 from tables (0.01) = 4.541

Element	Measured value $\mu g\ g^{-1}$	Certified value $\mu g\ g^{-1}$	Recovery %	Calculated *t* value
Ti	95.4 ± 1.8	100.4 ± 3.8	95.0	-5.5
V	95.2 ± 1.8	95.9 ± 9.4	99.3	-0.7
Cr	77.7 ± 4.1	98.3 ± 0.8	79.1	-9.9
Ni	99.8 ± 1.9	99.7 ± 1.6	100.1	0.1
Cu	99.4 ± 1.5	100.0 ± 1.9	99.4	-0.3
Mo	94.9 ± 3.0	100.3 ± 1.4	94.7	-3.5
Sn	94.2 ± 2.6	97.2 ± 2.6	96.9	-2.2
Pb	85.8 ± 8.6	101.1 ± 1.3	84.8	-3.5

3.7 Calibration with aqueous standard solutions

Aqueous analyte solutions, containing increasing concentrations of multielement standards (0.1, 1.0, 10 and 100 ng ml^{-1})were analysed and good calibration curves were obtained. These curves enabled correlation between analyte signal of the specimen microemulsion and the signal of the analyte solutions. Tables 14&15, show good agreement between the results of both CRMs (1084a and HU-1) obtained by calibration with inorganic aqueous standards and others obtained by calibration with emulsified standards. A paired t-test was applied (comparing results from the emulsified standard solution with those from the aqueous standard solutions for both CRMs HU-1 and 1084a) and it was found that the calculated t values for Tables 14&15 were t = 2.734 and 2.677 respectively. These values were less than the t values from the table $t_{v=7}(0.01)$ = 2.998 confirming that there was no significant difference between the two types of standard solutions used [81].

Both tables demonstrate very good agreement between the results obtained using the aqueous simple standard solutions and the certified values. Despite the difference in sample matrix between the aqueous standards used for calibration and the emulsified samples, the aqueous standard solutions can be used successfully at least as a rough guide to give an idea about trace elements content in the sample or it can also be used effectively in semiquantitative analysis.

Table 14 Comparison between CRM HU-1 microemulsion results obtained from calibration with aqueous standard solution and results obtained from calibration with emulsified standard solution

Element	Aqueous Standard Solution $\mu g\ g^{-1}$	Emulsified Standard Solution $\mu g\ g^{-1}$	C.V $\mu g\ g^{-1}$
Ti	13.0 ± 0.8	10.7 ± 1.5	9 ± 2
V	7.9 ± 0.6	7.5 ± 0.6	7 ± 0.5
Cr	13.2 ± 5.6	12.7± 6.8	15 ± 2
Mn	18.2 ± 1.1	18.0 ± 1.4	18 ± 1
Ni	46.3 ± 1.8	45.5 ± 3.7	45 ± 3
Mo	13.1 ± 1.0	12.4 ± 0.9	11 ± 1
Cd	16.8 ± 1.8	15.7 ± 1.5	15 ± 1
Pb	20.0 ± 1.7	20.1 ± 1.9	20 ± 1

Table 15 Comparison between CRM 1084a microemulsion results obtained from calibration with aqueous standard solution and results obtained from calibration with emulsified standard solution

Element	Aqueous Standard Solution $\mu g\ g^{-1}$	Emulsified Standard Solution $\mu g\ g^{-1}$	C.V $\mu g\ g^{-1}$
Ti	103.1 ± 1.6	95.4 ± 1.8	100.4 ± 3.8
V	102.8 ± 1.7	95.2 ± 1.8	95.9 ± 9.4
Cr	91.02 ± 5.4	77.7 ± 4.1	98.3 ± 0.8
Ni	104.7 ± 2.5	99.8 ± 1.9	99.7 ± 1.6
Cu	100.4 ± 2.4	99.4 ± 1.5	100.0 ± 1.9
Mo	100.3 ± 2.4	94.9 ± 3.0	100.3 ± 1.4
Sn	91.5 ± 1.0	94.2 ± 2.6	97.2 ± 2.6
Pb	89.9 ± 3.5	85.8 ± 8.6	101.1 ± 1.3

3.8 Real Samples Results

In order to assess the analytical capability of the proposed method, three Libyan crude oil samples were investigated for their trace elements content using microemulsion formation. El-Bouri, El-Sharara and Amna crude oils were emulsified using the proposed procedure (section 2.3.4) by dissolving the oils in tetralin then adding Triton X-100 , 5 ml of water, and 20 $\mu g\ L^{-1}$ of indium as an internal standard followed by 0.1 % nitric acid. Table 16, displays the concentration of Ti, V, Ni, Cu, Mo, Mn, Cd, Sn and Pb in the El-Bouri, El-Sharara and Amna samples. El- Bouri crude oil was found to contain 22.2 $\mu g\ g^{-1}$ vanadium and 20.1 $\mu g\ g^{-1}$ nickel with a trace of cadmium (0.02 $\mu g\ g^{-1}$), while Ti, Mn, Cu, Mo, Sn and Pb were below the detection limit of the instrument. The El-Sharara crude oil was found to contain 0.79 $\mu g\ g^{-1}$ of vanadium while the other selected elements were below the detection limit. Amna crude oil, contained 0.6 $\mu g\ g^{-1}$ vanadium, 0.05 $\mu g\ g^{-1}$ manganese,
2.1 $\mu g\ g^{-1}$ nickel and 0.3 $\mu g\ g^{-1}$ lead, while the other elements concentration was below the detection limit. The low levels of these elements reflect the high quality of Libyan crude oils, which make them suitable for the European market [79]. These oils do not contain high amounts of impurities, which require difficult and very expensive refinery processes to get rid of the elements. For example, Venezuelan crude oil contains 1400 $\mu g\ g^{-1}$ of vanadium [80] which is undesirable as it deactivates the catalysts used in refineries, and causes corrosion in the refinery boilers and furnaces.

Table 16 . Mean of trace elements concentration in emulsified Libyan crude oil samples in $\mu g\ g^{-1}$ ± standard deviation; number of replicates (n= 5)

Element	El-Bouri $\mu g\ g^{-1}$	El-Sharara $\mu g\ g^{-1}$	Amna $\mu g\ g^{-1}$
Ti	< 0.7	< 0.7	< 0.7
V	22.2 ± 1.1	0.79 ± 0.07	0.6 ± 0.02
Mn	< 0.1	< 0.1	0.05 ± 0.01
Ni	20.1 ±1.4	< 0.1	2.1 ± 0.12
Cu	< 0.2	< 0.2	< 0.2
Mo	< 0.1	< 0.1	< 0.1
Cd	0.02 ± 0.3	< 0.1	< 0.1
Sn	< 0.6	< 0.6	< 0.6
Pb	< 0.1	< 0.1	0.3 ± 0.04

The nickel and vanadium results obtained for El-Bouri, El-Sharara and Amna were confirmed by wet digestion, dry ash and microwave digestion and the results are shown in Table 17. Comparison of the results obtained indicates that there is very good agreement between the four methods. With regard to the vanadium results, the agreement between the four methods was close apart from the El-Bouri dry ash method (17.5 $\mu g\ g^{-1}$ compared to 22.4 $\mu g\ g^{-1}$). With regard to the nickel results, also there was agreement between the four methods although the El-Bouri dry ash method

gave a slightly lower result than those for the other methods. In El-Sharara crude oil, the wet digestion and the emulsion methods quote results that were below the detection limit. In contrast, the results for the other two methods were slightly higher. Amna crude oil results, exhibited good agreement between the four methods.

A statistical F-Test was applied (comparing the microemulsion results with the wet digestion results, in the order shown in Table 17) and the calculated F values were 2.67, 2.04, 4.93, 1.65 and 2.93 which were less than the F value from the table $F_{5,5}$ (0.05) = 5.05. The results proved that the variances between the results are likely to be the same [81].

Table 17. Comparison between the mean concentration of nickel and vanadium in three Libyan crude oil samples prepared with microemulsion, wet digestion, dry ash and microwave digestion in $\mu g\ g^{-1}$ ± standard deviation

Element	Sample	Wet digestion $\mu g\ g^{-1}$	Dry Ash $\mu g\ g^{-1}$	Microemulsion $\mu g\ g^{-1}$	Microwave $\mu g\ g^{-1}$
V	El-Bouri	22.4 ± 1.8	17.5 ± 0.1	22.2 ± 1.1	22.0 ± 0.8
	El-Sharara	0.5 ± 0.1	0.40 ± 0.02	0.79 ± 0.07	0.5 ± 0.02
	AMNA	0.24 ± 0.08	0.20 ± 0.01	0.6 ± 0.02	0.25 ± 0.01
Ni	El-Bouri	23.8 ± 1.8	15.0 ± 0.01	20.1 ±1.4	19.8 ± 1.0
	El-Sharara	< 0.05	0.1 ± 0.2	< 0.1	0.6 ± 0.2
	AMNA	2.8 ± 0.07	2.0 ± 0.1	2.1 ± 0.1	2.7 ± 0.4

It can be seen from the previous results that there is a variation in nickel and vanadium concentrations in different crude oil samples from different basins in Libya. The resultant vanadium / nickel ratios do not change with the biodegradation or weathering of an oil seep. Therefore, this ratio can be used as a fingerprint in order to link the crude oil to its geographic origin. This enables matching oil spills to their origin even after many years.

Chapter 4

4.1 Conclusion

In the present study, a simple analytical method for the determination of Ti, V, Cr, Mn, Ni, Cu, Mo, Cd, Sn, and Pb in crude oils by ICP-MS was developed. Samples were emulsified and introduced into the plasma as microemulsions. The experimental parameters were optimized to enable the sensitive, accurate and precise determination of these elements in crude oil samples. Calibration curves were established using tetralin and Triton X-100 employing analyte inorganic standards and In as an internal standard. The limits of detection and quantification were in the ng g^{-1} range.

Two certified reference materials (HU-1 used oil and 1084a wear metals in lubricating oil) were emulsified and introduced into the plasma in order to estimate the accuracy of the method. The results were compared with those obtained from dry ash, wet digestion and microwave digestion and found to be satisfactory. In order to evaluate the accuracy of the method, a spike recovery test was carried out and good results were obtained. The two emulsified reference materials (HU-1 used oil and 1084a) were analysed using aqueous standards and the results were compared with those obtained by calibration with emulsified standards. Three Libyan crude oil samples were analysed using the proposed methodology and the results were compared with the traditional ones (dry ash, wet digestion and microwave digestion). Very good agreement between the four methods was achieved.

In this study, a transparent stable microemulsion was used successfully without the need for an oxygen stream and no carbon build up was observed. The stability of the microemulsion lasted more than three months without phase separation or any change in appearance. Furthermore, microemulsion sample introduction was found to be a very effective technique for the determination of trace elements in crude oil. The major advantage of the microemulsion approach was that it is less time consuming. It presents the possibility of highly sensitive analysis which does not require decomposition, and allows the use of inorganic standards. Any potential loss of analyte elements due to volatilization or precipitation during the decomposition procedure is eliminated. The probability of introducing contamination is also reduced.

4.2 Recommendations

Identifying the gaps in knowledge on the stability and homogeneity of the formed microemulsion is an essential part of this study. Therefore, the following recommendations for further research are suggested:

First, a considerable amount of work still needs to be done to ensure the suitability of the depicted technique for the other fractions of crude oil, especially the light fractions such as the naphtha. This should focus on the effect of temperature on the stability of some volatile analytes such as mercury in the formed microemulsion.

Second, it would be beneficial to measure the size of the microemulsion droplets formed with the proposed method. Further studies on the effect of heat and sonication on the emulsion droplet size are also recommended because the stability of the micoemulsion increases with the decrease in the emulsion droplet size.

Third, a comparison between detergent and detergentless microemulsions using different spectrometric techniques, in terms of stability and the quality of the results is highly recommended.

Fourth, it would be useful to study the chemical composition of crude oils before and after the emulsification and to investigate any possible changes that may occur because of the presence of an oxidising agent.

Fifth, applying different acids or a mix of some acids such as HCl and HNO_3 , in order to acidify the microemulsion could give further knowledge on the stability of the analytes of interest in the microemulsion. In addition, employing hydrogen

peroxide instead of HNO_3 , may provide information to help improve the stability of the microemulsion, and consequently the quality of the obtained data.

Sixth, as the choice of the surfactant has a main role in the stability of the prepared microemulsion, studying the possibility of applying mixed surfactants, non-ionic and anionic, will be very useful and may lead to new knowledge on crude oil microemulsion formation.

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Appendix A

Table 1. Summary for the emulsification procedures discussed in the literature review

Ref. No.	Sample Type	Instrument Used	Elements Determined	Emulsion Type	Emulsion Composition	Addition of HNO_3	Period of Stability
43	Gasoline	FAAS	Pb	Surfactant	1ml S* + 20 ml H_2O + 5 drops of Emulsifier		1 h
44	Gasoline	FAAS	Mn	Surfactant	10 ml S + 1.5ml Br_2CCl_4 + H_2O + 4 ml Emulsogen		2 months
45	Crude Oil	FAAS	V, Ni, Fe, Mg, Na	Detergentless	3g S+ 15 ml Ethanol +0.3 ml(10%) LASA*		
17	Gasoline & Kerosene	ETAAS	As, Se, Sb	1) Detergentless 2) Surfactant	1.a) Gasoline: 10 % S+ 25 %H_2O +65%propanol 1.b)Kerosene: 10 % S+ 15 %H_2O +75%propanol 2) 10 % S+ 4 % Triton X-100	1ml conc. HNO_3	10 min
46	Kerosene	ETAAS	Pb, Cu	Detergentless	5 ml S + 11 ml propanol	2 ml conc. HNO_3	24 h
47	Lubricating Oils	FIETAAS	Cr	Surfactant	S+ SDS + Hexan		
32	Used Lubricating Oils	ETAAS	Ag	Surfactant	0.2 g S + 0.5 ml xylene + 0.4 ml TritonX-100	0.5 ml conc. HNO_3	30 min
48	Used Lubricating Oils	ETAAS	Sb, Sn	Surfactant	0.2 g S + 0.5 ml xylene + 0.4 ml TritonX-100	0.5 ml conc. HNO_3	30 min
49	Gasoline	ETAAS	Cu, Co, Pb	Detergentless	1ml S + 2.5 ml H_2O + 96 % ethanol	0.5 ml conc. HNO_3	Long Term Stability
50	Diesel & Gasoline	ETAAS	Ni, Pb	Detergentless	3..3 ml S +6.5 ml propanol	1 ml 50% HNO_3	15 days
52*	Lubricating Oils	ETAAS	Al	Surfactant	0.5 ml S +1 ml Secbutanol + 1 ml Surfactant		One month

S = Sample, LASA=Linear alkylbenzene sulfonic acid, E=Emulsion, B= Butter, M= Margarine

53	Lubricating Oils	ICP-OES	Ni, Mo, Cr, V, Ti	Surfactant	0.2 ml S + 0.5 ml xylenre + 0.6 ml TritonX-100	0.5 ml conc. HNO_3	40 min
54	Crude Oil	ICP-OES	Mo, Zn, Cd,Ti, Ni, V, Fe, Mn, Cr, Co	Detergentless	0.6 g S + 0.5 ml xylene + propanol +H_2O	0.4 ml conc. HNO_3	One week
55	Diesel & Fuel Oil	ICP-OES	Mo, Cr, V, Ti	1) Detergentless 2) Surfactant	1) 2.5g S + 6 ml propanol + H_2O 2) 1.5 g S + xylene + 0.3 ml TritonX-100 + H_2O	0.5 ml conc. HNO_3	Milky separates Shortly
56	Olive & Soy Oil, Butter & Margarine	ICP-OES	Cd, Co Cr, Cu, Ni, Mn	1) Detergentless 2) Surfactant	1) 0.1g S + 7 g propanol 2) 0.2 g S + 0.2 g TritonX-100	0.5 ml conc. HNO_3	3 min doesn't form E* for B* & M*
24	Crude Oil	ICP-MS	Li, Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Pb	Surfactant	0.5 g S + 0.5 g tetraline + 1 g Triton X-100+H_2O		3 months
10	Crude Oil	SIA/ICP-MS	Pb, Ni, V	Surfactant	0.5 g S + 1.5 ml tetraline + 0.5 ml Triton X-100		
57	Crude Oil	ICP-MS	Ni, V	Surfactant	0.5 g S + 0.5 g tetraline +1 g Triton X-100	5 ml 40 % HNO_3	
22	Naphtha	ICP-MS	V, Vo, Ni, As, Hg, Pb	Surfactant	2 ml S + 1 ml 2.5 % Triton X-100		
38	Gasoline	ETV/ICP-MS	Cu, Mn, Ni, Sn	Surfactant	60 % S + 4 % Triton X-100	1 ml conc. HNO_3	
58	Gasoline	ICP-MS	S	Surfactant	0.5 g S + 0.5 g tetraline + 1 g Triton X-100+H_2O		
59	Olive Oil	ICP-MS	Ba, Cd, Co, Cr, Cu, Mn, Ni, Tl, Pb, U, V,Zn	Surfactant	2 g S + 1.5 ml TritonX-100	HNO3 Not recomm en-ded	